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# Recent advances in noble metal-free electrocatalysts to achieve efficient alkaline water splitting

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Electrochemical water splitting is one of the promising approaches for generating hydrogen. Developing noble metal-free electrocatalysts for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) is important to achieve efficient water-splitting. This paper reviews the activity, stability, and durability of recently reported noble metal-free electrocatalysts such as oxides/hydroxides/(oxy)hydroxides/layered double hydroxides, sulfides, selenides, phosphides/phosphates, nitrides, carbon-based electrocatalysts, and alloy/B/V/F/Si based electrocatalysts for the HER and OER in an alkaline environment, including the strategies used to achieve high activity and stability/durability at a current density of  $\geq 1000$  mA cm<sup>-2</sup>. Moreover, this paper discusses the various promising strategies including the fabrication of nanostructured, ultrathin, porous, and nanoporous materials, preparing superhydrophobic surfaces, construction of hollow structures, core-shell structures, heterostructures, heterojunctions, or Mott-Schottky heterojunctions, designing facile and/or scalable synthesis routes, creating doping and/or vacancies/defects, fabricating catalysts with high valence state sites, designing medium or high-entropy alloys, and tuning the atomic packing structure, electronic structure, or conductivity to enhance the activity and stability for the HER and/or OER.

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## 1. Introduction

Hydrogen is considered as a promising fuel having low carbon emission and high energy density (142 MJ kg<sup>-1</sup>). The global hydrogen production market size was estimated at about 120 billion USD in the year 2020, whereas currently, about 95% of the industrial hydrogen production processes such as steam reforming, and coal gasification with extensive greenhouse gas release are not efficient processes, while only about 4% of the

H<sub>2</sub> production around the world depends on water electrolysis, and the current research studies are being focused on water electrolysis or other strategies to alleviate the utilization of fossil fuels for the production of hydrogen energy.<sup>1</sup> Electrochemical water splitting is a promising way for sustainable hydrogen production, especially with renewable electricity such as solar or wind sources.<sup>2</sup> Electrochemical water splitting comprises a hydrogen evolution reaction (HER) at the cathode with the involvement of two electrons, and an oxygen evolution reaction (OER) at the anode with the involvement of four electrons in both acid and alkaline environments. Currently, noble electrocatalysts, such as Ir/Ru-based compounds for the OER and Pt for the HER, are considered as promising electrocatalysts for water splitting.<sup>3</sup> Nevertheless, their high cost and scarcity limit their uses. Moreover, the currently used OER electrocatalysts for water splitting in acid environments are scarce and expensive,<sup>3,4</sup> whereas the cost of the water electrolyzer system can be reduced by using noble metal-free electrocatalysts in the alkaline environment.<sup>2b,d,5</sup> To alleviate the gas mixing issues (H<sub>2</sub> and O<sub>2</sub>), proton exchange membrane (PEM) water electrolysis and anion exchange membrane (AEM) water electrolysis are considered as promising water electrolyzers for industrial level application, where the AEM water electrolyzer can operate in an alkaline environment but the PEM water electrolyzer may require acid-stable OER

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electrocatalysts to operate in an acid environment, which can elevate the cost.<sup>6</sup> Therefore, various promising strategies such as improving the gas-evolution behavior, enhancing the conductivity, tuning the electronic structure, increasing the electrochemical surface area, surface reconstruction during the HER/OER, preparing core-shell/hetero/hollow structured materials, preparing amorphous materials, fabricating bimetallic/multi-metallic materials, doping metals/heteroatoms, preparing porous/nanostructured/quantum sized materials, and creating oxygen vacancies/defects are used to achieve high-performance noble metal-free electrocatalysts for the HER and/or OER in an alkaline environment.<sup>5,7</sup>

Developing noble-metal-free electrocatalysts with substantially lower overpotential ( $\eta$ ) for HER and OER or significantly lower cell voltage for overall water splitting is highly desirable. Fabrication of transition metal boride electrocatalysts with a 3D hollow structure may alter the electronic structure, provide optimal adsorption energy with intermediates, improve the conductivity, expose abundant active sites, provide high mechanical strength, and facilitate gas evolution, all of which could improve the activity and stability of the HER and OER. For the HER in 1 M KOH, NiMoB hollow foam<sup>8</sup> affords an  $\eta$  of  $-18$  mV at  $-10$  mA cm<sup>-2</sup>, suggesting its outstanding activity. For overall water splitting in 1 M KOH, NiMoB hollow foam//NiMoB hollow foam affords a potential of 1.431 V at 10 mA cm<sup>-2</sup>, suggesting its good activity. Fabrication of composites containing transition metal selenides and perovskite oxides could enhance the performance of the OER. For the OER in 1 M KOH, LSCO-MoSe<sub>2</sub> (ref. 9) affords an  $\eta$  of 39 mV at 10 mA cm<sup>-2</sup>, suggesting its very high activity, where LSCO is La<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3- $\delta$</sub>  perovskite oxide. Moreover, Mn<sub>1</sub>Ni<sub>1</sub>Co<sub>1</sub>-P//Mn<sub>1</sub>Ni<sub>1</sub>Co<sub>1</sub>-P,<sup>10</sup> c-NiFe/a-NiFeOOH@NiMo//c-NiFe/a-NiFeOOH@NiMo,<sup>11</sup> and Gr-CNTs-Sn<sub>4</sub>P<sub>3</sub>//Gr-CNTs-Sn<sub>4</sub>P<sub>3</sub> (ref. 12) exhibit very high activity for overall water splitting in 1 M KOH, while the NiP<sub>2</sub>-FeP<sub>2</sub>@Cu nanoarray<sup>13</sup> exhibits very high activity for the HER. Thus, several noble metal-free electrocatalysts exhibit substantially much lower  $\eta$  for the HER and OER or significantly much lower cell voltage for overall water splitting.

An electrocatalyst for the HER or OER fabricated at a relatively low cost should operate at low  $\eta$  to deliver a current density for a prolonged period, which is highly desirable for industrial applications. Fabrication of tin-doped nickel sulfide having an ultrathin nanostructure could modify the electronic structure, and facilitate the evolution of gas even at large current densities, and that could boost the performance of the HER and OER. For the OER in 1 M KOH, the Sn-Ni<sub>3</sub>S<sub>2</sub> (ref. 14) affords an  $\eta$  of 267 mV at 100 mA cm<sup>-2</sup>, and an  $\eta$  of 580 mV at a current density of 1000 mA cm<sup>-2</sup>, indicating its significantly high activity, while it undergoes negligible decay at a very large current density of 2000 mA cm<sup>-2</sup> after 10 000 cycles of CV, suggesting its substantially good durability. For the HER in 1 M KOH, it affords an  $\eta$  of  $-171$  mV at  $-100$  mA cm<sup>-2</sup>, and an  $\eta$  of  $-570$  mV at a current density of  $-1000$  mA cm<sup>-2</sup>, suggesting its

significantly very high activity, while it undergoes negligible decay at a current density of  $-1000$  mA cm<sup>-2</sup> after 10 000 cycles of CV, suggesting its significantly very high durability. For overall water splitting in 1 M KOH, the Sn-Ni<sub>3</sub>S<sub>2</sub>//Sn-Ni<sub>3</sub>S<sub>2</sub> affords a potential of 1.46 V at 10 mA cm<sup>-2</sup>, and  $\sim 2.65$  V at a current density of 1000 mA cm<sup>-2</sup>, suggesting its significantly very high activity. Integrating N-doped carbon with nanostructured transition metal/metal oxide could redistribute the electrons at the heterojunction interface, afford optimal adsorption energy with intermediates, enhance the conductivity, facilitate the evolution of gas, expose abundant active sites, and that could enhance the performance for the HER and OER. For the OER in 1 M KOH, Ni/MoO<sub>2</sub>@CN<sup>15</sup> affords an  $\eta$  of 250 mV at 10 mA cm<sup>-2</sup>, and an  $\eta$  of 420 mV at a large current density of 1000 mA cm<sup>-2</sup>, suggesting its significantly very high activity, while it undergoes negligible decay at a large current density of 1000 mA cm<sup>-2</sup> for 200 h, suggesting its significantly very high stability. For the HER in 1 M KOH, it affords an  $\eta$  of  $-33$  mV at  $-10$  mA cm<sup>-2</sup>, and an  $\eta$  of  $-267$  mV at a large current density of  $-1000$  mA cm<sup>-2</sup>, suggesting its significantly very high activity, while it undergoes negligible decay at a large current density of  $-1000$  mA cm<sup>-2</sup> for 200 h, suggesting its significantly very high stability. For overall water splitting in 1 M KOH, Ni/MoO<sub>2</sub>@CN//Ni/MoO<sub>2</sub>@CN affords a potential of 1.83 V at 200 mA cm<sup>-2</sup>, and a potential of 2.02 V at a large current density of 1000 mA cm<sup>-2</sup>, suggesting its significantly very high activity, while it affords 98.19% retention at 1.7 V for 168 h, suggesting its significantly very high stability. Moreover, C-Ni<sub>1-x</sub>O/3D printed Ni,<sup>16</sup> Fe-Co-CO<sub>3</sub>-OH,<sup>17</sup> FeP/Ni<sub>2</sub>P,<sup>18</sup> Ni<sub>2</sub>P-Fe<sub>2</sub>P,<sup>19</sup> and Co<sub>2</sub>N<sub>0.67</sub>/CoMoO<sub>4</sub> (ref. 20) for the HER and OER exhibit high activity and stability in 1 M KOH, while MoS<sub>2</sub>/Mo<sub>2</sub>C<sup>21</sup> for the HER, and CuS-Ni<sub>3</sub>S<sub>2</sub>/CuNi<sup>22</sup> for the OER exhibit high activity and stability. Thus, several noble metal-free electrocatalysts exhibit low  $\eta$  at high current densities with high stability for the HER and OER.

Besides, the fabrication of noble metal-free electrocatalysts by green-chemistry approaches is highly desirable to achieve efficient, green water electrolysis, and that could alleviate or diminish the use or production of hazardous substances.<sup>23</sup> Designing energy-efficient synthesis routes (especially at room temperature) for the fabrication of noble metal-free electrocatalysts is one of the promising green-chemistry approaches.<sup>23</sup> Chen *et al.*<sup>24</sup> observed that S-FeOOH exhibits enhanced activity and stability for the OER, while it was obtained by immersing cleaned Fe foam for 20 min at room temperature in the solution containing Fe(NO<sub>3</sub>)<sub>3</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. The redox reactivities of the lattice oxygen and Fe in FeOOH are activated due to S doping. Moreover, Zhao *et al.*<sup>25</sup> observed that NiFe LDH exhibits enhanced activity and stability for the OER, while it was prepared by immersing cleaned, acid-treated Fe foam in NiSO<sub>4</sub> solution under ambient conditions. In addition, Liu *et al.*<sup>26</sup> observed that IronCE10s exhibit enhanced activity and stability for the OER, while it was prepared on the cheap iron substrate by applying pulsed potentials for 10 s in



NiSO<sub>4</sub> electrolyte at 25 ± 1 °C, where the substrate was used as a counter electrode. The utilization of waste as a source for the fabrication of noble metal-free electrocatalysts is one of the promising green chemistry approaches.<sup>23</sup> Lu *et al.*<sup>27</sup> observed that WO<sub>3</sub>@F<sub>0.1</sub>-C exhibits enhanced activity and stability for the OER, while it was obtained by a plasma-induced assembly method, where perfluorooctanoic acid (a pollutant) is used as an F source. Utilization of renewable raw materials for the fabrication of noble-metal-free electrocatalysts is one of the most promising green-chemistry approaches.<sup>23</sup> Huang *et al.*<sup>28</sup> observed that Zn-Fe/Mn@Mn-FeP exhibits enhanced activity and stability for the HER and OER, where the nanostructured phosphide-based electrocatalyst is prepared using relatively low-cost metals such as Fe, Mn, and Zn. Thus, some green chemistry approaches including ambient temperature synthesis, utilization of waste as a source, and using relatively low-cost metals have been used for the fabrication of noble metal-free electrocatalysts for electrochemical water splitting.

Thus, recently, several promising strategies have been used for the fabrication of noble metal-free electrocatalysts to achieve low  $\eta$  at high current densities with high stability for the HER and OER and to achieve substantially much lower  $\eta$  for the HER and OER, while some green chemistry approaches have been applied for the fabrication of noble metal-free electrocatalysts for electrochemical water splitting. However, reviews on the fabrication of various noble metal-free electrocatalysts using several promising strategies along with their catalytic performances for electrochemical water splitting (HER and OER) in alkaline environments have been rarely reported. In this respect, the present paper reviews the activity, stability, and durability of several kinds of recently reported noble metal-free electrocatalysts such as oxides/hydroxides/(oxy)hydroxides/layered double hydroxides, sulfides, selenides, phosphides/phosphates, nitrides, carbon-based electrocatalysts, and alloy/B/V/F/Si based electrocatalysts for the HER and OER in an alkaline environment. In addition, this paper reviews the strategies used to achieve high activity and stability/durability at a current density of  $\geq 1000$  mA cm<sup>-2</sup> of noble metal-free electrocatalysts for the HER and OER in an alkaline environment. Moreover, this paper reviews some green chemistry approaches used for the fabrication of noble metal-free electrocatalysts for electrochemical water splitting. Finally, this review summarizes several promising strategies used for the fabrication of noble metal-free electrocatalysts to achieve enhanced performance for the HER and OER in alkaline environments.

## 2. Constructing noble metal-free electrocatalysts for the HER and OER in an alkaline electrolyte

### 2.1. Constructing oxide/hydroxide/(oxy)hydroxide/layered double hydroxide electrocatalysts

**2.1.1. Constructing oxide electrocatalysts.** Fabrication of nanostructured transition metal oxides could expose abundant active sites, facilitate the evolution of gas, and that could

enhance the performance of the HER and OER. Chen *et al.*<sup>29</sup> observed that Co<sub>3</sub>O<sub>4</sub> exhibits enhanced activity and stability for the HER and OER. It was prepared on Co foam by sulfuration at 350 °C for 30 min followed by *in situ* electrochemical oxidation for 2 h. It is composed of a cubic Co<sub>3</sub>O<sub>4</sub> phase. It possesses microspheres, which are composed of nanosheets. For overall water splitting in 1 M KOH, Co<sub>3</sub>O<sub>4</sub>//Co<sub>3</sub>O<sub>4</sub> affords a potential of 1.483 V at 10 mA cm<sup>-2</sup>, suggesting its very high activity.

Fabrication of nanostructured transition metal oxide/metal heterojunctions could expose abundant active sites, facilitate the evolution of gas, afford optimal adsorption energy with intermediates, and that could enhance the performance of HER and OER. Guo *et al.*<sup>30</sup> observed that MoO<sub>2</sub>/Co exhibits enhanced activity for the HER and OER. It was synthesized on Ni foam by hydrothermal treatment followed by annealing under a H<sub>2</sub>/Ar atmosphere. MoO<sub>2</sub>/Co exhibits higher activity and lower charge transfer resistance for the HER than the CoMo precursor. It is crystalline containing MoO<sub>2</sub>,  $\alpha$ -Co, and  $\beta$ -Co phases having heterojunction. It contains Mo, Co, and O, which are homogeneously distributed. It possesses an ultrathin porous nanosheet structure. The density functional theory (DFT) calculations reveal that the Gibbs free energy of hydrogen adsorption ( $\Delta G_{H^*}$ ) of MoO<sub>2</sub>/Co (-0.38 eV) is much nearer to the thermoneutral value than pure Co (-1.46 eV), suggesting the optimal hydrogen adsorption/desorption on the MoO<sub>2</sub>/Co heterojunction, and that could enhance the activity for the HER. The HER in 1 M KOH affords an  $\eta$  of -48 mV at -10 mA cm<sup>-2</sup>, suggesting its very high activity. Fabricating nanostructured transition metal doped metal oxides with oxygen vacancies could provide optimal adsorption energy with intermediates, and that could boost the performance of the HER and OER. Xue *et al.*<sup>31</sup> observed that Mn<sub>6</sub>-CoO exhibits enhanced activity and stability for the HER and OER. It was obtained on Ni foam by hydrothermal treatment followed by annealing at 350 °C for 2 h under an Ar atmosphere. Mn<sub>6</sub>-CoO exhibits higher activity for the HER and OER than CoO, while it exhibits higher electrochemical surface area and lower charge transfer resistance than CoO. Mn<sub>6</sub>-CoO is composed of Mn-doped CoO. It possesses a heterophase (amorphous-crystalline). It contains oxygen vacancies (38.2%). It possesses a rambutan-like morphology, which contains numerous small nanoneedles. The DFT calculations reveal that the oxygen vacancies in Mn-CoO can optimize the adsorption-free energy of H\* and HOO\* intermediates, suggesting enhanced performance for the HER and OER. The HER in 1 M KOH affords an  $\eta$  of -25.6 mV at -10 mA cm<sup>-2</sup>, suggesting its significantly very high activity. For overall water splitting in 1 M KOH, Mn<sub>6</sub>-CoO//Mn<sub>6</sub>-CoO affords a potential of 1.52 V at 10 mA cm<sup>-2</sup>, suggesting its very high activity.

Rani *et al.*<sup>32</sup> studied the fabrication of faceted transition bimetallic oxide (CuMn<sub>2</sub>O<sub>4</sub>) nanoparticles with oxygen vacancies which can enhance the performance, activity, and stability of the HER. It was prepared by the polyol-mediated annealing method (hydrothermal treatment followed by annealing at 600 °C). The reported activity of faceted CuMn<sub>2</sub>O<sub>4</sub> is higher than that of non-faceted CuMn<sub>2</sub>O<sub>4</sub> for the HER. The prepared sample showed a cubic spinel CuMn<sub>2</sub>O<sub>4</sub> phase, and Mn, Cu, and O are homogeneously distributed. It also has oxygen vacancies. HER



active phases can be produced by tuning the calcination parameters such as temperature, gas atmosphere, and time. Wu *et al.*<sup>33</sup> observed that Bi<sub>2</sub>O<sub>3</sub>-based catalyst exhibits enhanced activity and stability for the HER. It was prepared on Ni foam by hydrothermal treatment followed by heat treatment at 400 °C for 2 h in air followed by heat treatment at 400 °C in an Ar/H<sub>2</sub> atmosphere. It is crystalline containing  $\alpha$ -Bi<sub>2</sub>O<sub>3</sub>, Bi<sub>3</sub>Ni, and BiNi alloys, which are homogeneously distributed. It possesses nanosheet morphology. Thus, applying an *in situ* phase engineering strategy for Bi<sub>2</sub>O<sub>3</sub> on Ni foam could produce HER active sites (Bi<sub>x</sub>Ni alloys and oxide phases), and that could enhance the performance of the HER.

Dynamically restructuring Ni<sub>x</sub>Cr<sub>y</sub>O during electrolysis enhanced the porosity for better activity of the OER. Malek *et al.*<sup>34</sup> fabricated Ni<sub>x</sub>Cr<sub>y</sub>O through hydrothermal treatment followed by calcination. The *in situ* and electrochemical investigations disclose that the electrochemically active surface area of Ni<sub>x</sub>Cr<sub>y</sub>O could be increased by the leaching and redistribution of Cr upon electrolysis for a certain time interval, leading to an increase in porosity, and that could enhance the activity for the OER. The OER in 1 M KOH affords an  $\eta$  of 270 mV at 100 mA cm<sup>-2</sup>, and an  $\eta$  of 320 mV at a high current density of 500 mA cm<sup>-2</sup>, suggesting its very high activity, while it affords high stability. Fabrication of ultrathin transition bimetallic oxides with abundant oxygen vacancies can afford optimal adsorption energy with intermediates to increase the conductivity, which could also improve the performance of the OER. Yu *et al.*<sup>35</sup> prepared f-Ni<sub>0.1</sub>Co<sub>0.9</sub>O<sub>x</sub> by the electron beam evaporation method followed by calcination at 160 °C for 30 min using an O<sub>2</sub> atmosphere under UV light irradiation. f-Ni<sub>0.1</sub>Co<sub>0.9</sub>O<sub>x</sub> exhibits higher activity, higher electrochemical surface area, and lower charge transfer resistance for the OER than f-CoO<sub>x</sub> and f-NiO<sub>x</sub>. The alloy oxide film (f-Ni<sub>0.1</sub>Co<sub>0.9</sub>O<sub>x</sub>) is optically transparent with a thickness of about 10 nm (ultrathin). It contains Co, Ni, and O, which are homogeneously distributed. It contains oxygen vacancies. Fabrication of a transition metal oxide/metal oxide hetero interface with abundant high valence ions can provide optimal adsorption energy with intermediates, increase the conductivity, and that could enhance the performance of the OER. Zhang *et al.*<sup>36</sup> observed that Co<sub>3-x</sub>O<sub>4</sub>/NiO exhibits enhanced activity and stability for the OER. It was prepared by hydrothermal treatment of the prepared Co<sub>3-x</sub>O<sub>4</sub> with nickel acetate followed by calcination in the air atmosphere. Co<sub>3-x</sub>O<sub>4</sub>/NiO exhibits higher activity, higher electrochemical surface area, and lower charge transfer resistance for the OER than Co<sub>3-x</sub>O<sub>4</sub> and Co<sub>3</sub>O<sub>4</sub>. It is crystalline containing Co<sub>3-x</sub>O<sub>4</sub> and NiO. It contains a heterointerface. It contains Co, Ni, and O, which are homogeneously distributed. It contains Ni<sup>3+</sup>, Ni<sup>2+</sup>, Co<sup>3+</sup>, and Co<sup>2+</sup>. It possesses particle morphology (diameter: about 20 nm). Fabrication of a thin layer of a transition metal oxide on ZnO can modulate the electronic structure, and that could enhance the performance of the OER. Nandanapalli *et al.*<sup>37</sup> observed that Co<sub>3</sub>O<sub>4</sub> SS Mesh/ZnO exhibits enhanced activity and stability for the OER (SS Mesh: stainless steel mesh).

It was obtained by atomic layer deposition followed by chemical bath deposition followed by annealing followed by electrochemical deposition. Co<sub>3</sub>O<sub>4</sub> SS Mesh/ZnO exhibits higher activity for the OER than SS Mesh/ZnO. It is composed of ZnO nanorods on stainless steel mesh, which are covered by a thin layer of cobalt oxide containing a predominant amount of Co<sub>3</sub>O<sub>4</sub> along with a minor amount of CoO. It is crystalline. It contains Zn, Co, and O, which are homogeneously distributed. It contains Co<sup>3+</sup> and Co<sup>2+</sup>.

Fabrication of nickel–molybdenum oxysulfide with unique morphology as a pre-catalyst is essential, where the electrochemical reduction of the pre-catalyst can produce a highly active robust catalyst containing metallic species for the HER, while the electrochemical oxidation of the pre-catalyst can form a highly active robust catalyst containing high valence species for the OER. Liu *et al.*<sup>38</sup> observed that the HR-NiMoO@Ni exhibits substantially very high activity and stability for the HER, while the OR-NiOOH exhibits significantly very high activity and stability for the OER. The NiMoOS pre-catalyst on Ni foam was synthesized by hydrothermal treatment followed by sulfurization at 350 °C for 2 h. HR-NiMoO@Ni was obtained by applying cathodic CV scans on NiMoOS, whereas OR-NiOOH was obtained by applying anodic CV scans on NiMoOS (CV: cyclic voltammetry). HR-NiMoO@Ni and OR-NiOOH exhibit higher electrochemical surface area and lower charge transfer resistance than NiMoOS. The NiMoOS pre-catalyst is crystalline and is composed of sulfur-doped nickel molybdate (NiMoO<sub>4</sub>). It contains Mo, Ni, O, and S, which are homogeneously distributed. It possesses nanorod array morphology. HR-NiMoO@Ni is composed of ultrathin cubic Ni metal nanosheets, which are vertically grown on NiMoO nanorods, forming a core–shell structure (core: NiMoO; shell: Ni). It contains abundant defects. OR-NiOOH is composed of quasi-crystalline NiOOH along with a residual amount of S. The atomic ratio of O: Ni: S is 3.9: 1.7: 0.1, respectively, suggesting the existence of a trace amount of S. It contains Ni<sup>3+</sup>. It contains abundant defects. It possesses nanorod array morphology. For the OER in 1 M KOH, it affords an  $\eta$  of 213 mV at 10 mA cm<sup>-2</sup>, and an  $\eta$  of 358 mV at a current density of 1000 mA cm<sup>-2</sup>, suggesting its significantly very high activity, while it affords reasonable stability at 1000 A m<sup>-2</sup> for 100 h, suggesting its significantly very high stability. For the HER in 1 M KOH, HR-NiMoO@Ni affords an  $\eta$  of -96 mV at -10 mA cm<sup>-2</sup>, and an  $\eta$  of -308 mV at a current density of -1000 mA cm<sup>-2</sup>, suggesting its substantially very high activity, while it affords reasonable stability at -1000 A m<sup>-2</sup> for 100 h, suggesting its significantly very high stability. For overall water splitting in 1 M KOH, OR-NiOOH<sup>OER</sup>//HR-NiMoO@Ni<sup>HER</sup> affords a potential of 1.51 V at 10 mA cm<sup>-2</sup>, suggesting its very high activity, while it affords reasonable stability at 1000 A m<sup>-2</sup> for 500 h, suggesting its significantly very high stability.

Designing a facile synthesis route for the fabrication of heterostructured transition metal oxides is essential, which



could modify the electronic structure, provide optimal adsorption energy with intermediates, and that could enhance the performance of the HER and OER. Hu *et al.*<sup>18</sup> observed that the MH-TMO (mesoporous and heterostructured transition metal oxides) exhibits enhanced activity and stability for the HER and OER than Fe<sub>2</sub>O<sub>3</sub>, and CuO. It was synthesized on Ni foam by one-step hydrothermal treatment. It is crystalline, containing Fe<sub>2</sub>O<sub>3</sub>, and CuO. It exhibits a heterostructure. The Fe 2p peak of MH-TMO exhibits a slight negative shift in the high-resolution XPS spectra which confirms the modified electronic structure. It contains oxygen vacancies and mesopores. It exhibits a slightly compressed M–O–M bond, suggesting the electronic interaction between Fe<sub>2</sub>O<sub>3</sub> and CuO. It possesses a sandwich structure, where the Fe<sub>2</sub>O<sub>3</sub> nanosheets are surrounded on either side by CuO polyhedra. The DFT calculations disclose that the Fe site on the MH-TMO heterostructure affords optimal adsorption energy with intermediates. For the OER in 1 M KOH, it affords an  $\eta$  of  $\sim 216$  mV at 10 mA cm<sup>-2</sup>, suggesting its very high activity, while it undergoes negligible decay at 10 mA cm<sup>-2</sup> for 100 h, suggesting its very high stability. For the HER in 1 M KOH, it affords an  $\eta$  of  $\sim -70$  mV at  $-10$  mA cm<sup>-2</sup>, suggesting its very high activity, while it affords reasonable stability at  $-10$  mA cm<sup>-2</sup> for 100 h. For overall water splitting in 1 M KOH, MH-TMO//MH-TMO affords a potential of 1.49 V at 10 mA cm<sup>-2</sup>, suggesting its very high activity, while it undergoes negligible decay at 10 mA cm<sup>-2</sup> for 100 h, suggesting its very high stability.

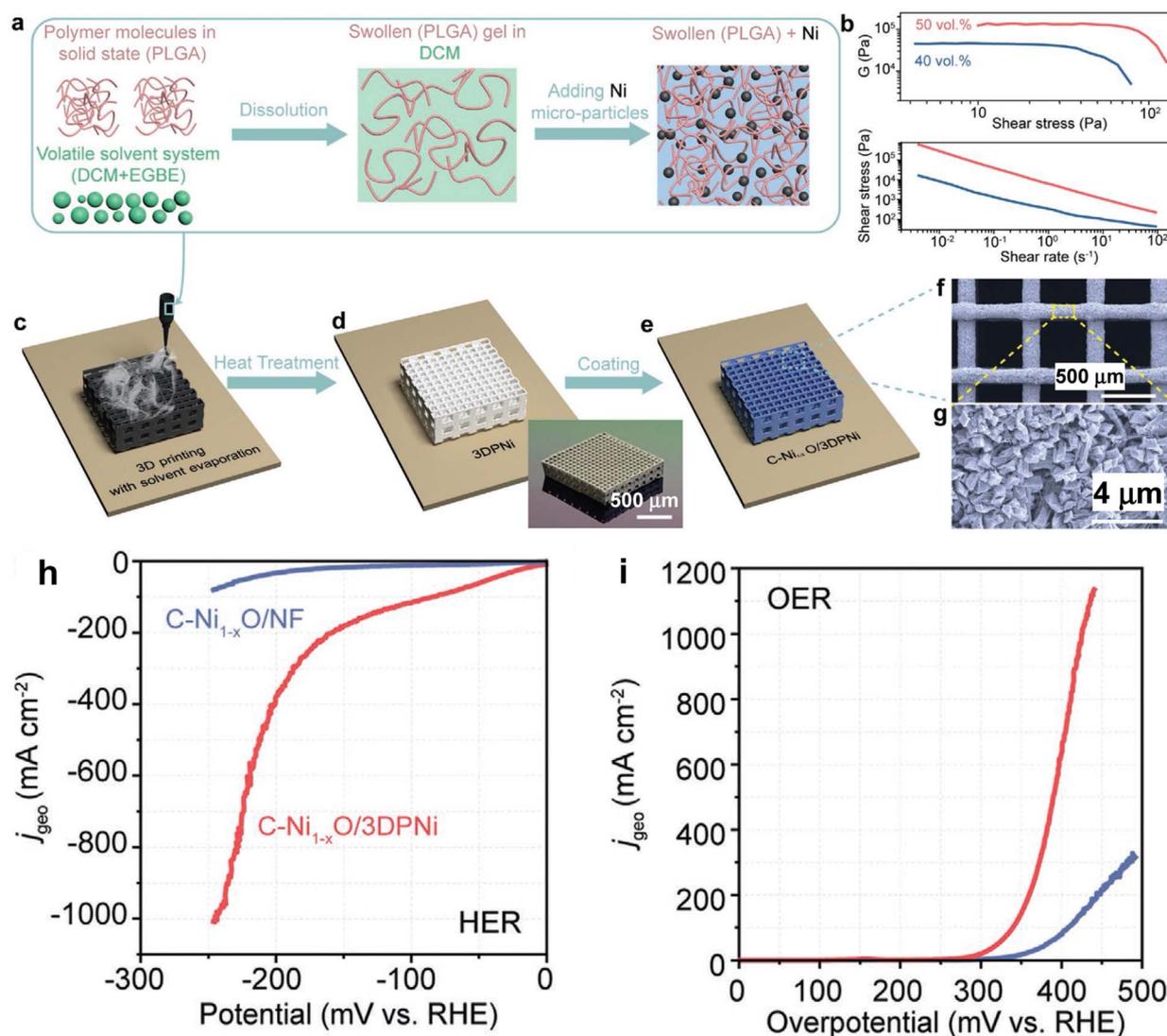
Fabrication of ultrafine transition metal oxide particles/nanostructured transition metal hydroxide heterostructures could modify the electronic structure, afford optimal adsorption energy with intermediates, and that could enhance the performance of the HER. Peng *et al.*<sup>39</sup> observed that MoO<sub>3</sub>-Co(OH)<sub>2</sub>@Ag exhibits enhanced activity and stability for the HER. It was prepared on Ag nanowire cloth by a two-step electrodeposition approach. MoO<sub>3</sub>-Co(OH)<sub>2</sub>@Ag exhibits higher activity, higher electrochemical surface area, and lower charge transfer resistance for the HER than MoO<sub>3</sub>@Ag and Co(OH)<sub>2</sub>@Ag. It is composed of a Co(OH)<sub>2</sub> nanosheet array on Ag nanowires, which is decorated by ultrafine MoO<sub>3</sub> particles. It is crystalline. It exhibits a heterostructure. In the high-resolution XPS spectra, the Mo 3d peak of MoO<sub>3</sub>-Co(OH)<sub>2</sub>@Ag exhibits a slight negative shift, when compared to that of MoO<sub>3</sub>@Ag, suggesting a modified electronic structure due to the electronic interaction between MoO<sub>3</sub> and Co(OH)<sub>2</sub>. It contains oxygen vacancies. The DFT calculations reveal that the Gibbs free-energy of the adsorbed H\* ( $\Delta G_{H^*}$ ) value on MoO<sub>3</sub>-Co(OH)<sub>2</sub> (0.22 eV) is nearer to 0 eV when compared to that of MoO<sub>3</sub> (0.71), and Co(OH)<sub>2</sub> (1.99), suggesting optimal hydrogen adsorption/desorption on the MoO<sub>3</sub>-Co(OH)<sub>2</sub> heterojunction.

Doping of phosphorus in cobalt molybdate could alter the electronic structure, provide optimal adsorption energy with intermediates, and that could enhance the performance of the HER and OER. Wang *et al.*<sup>40</sup> observed that P-CoMoO<sub>4</sub> exhibits enhanced activity and stability for the HER and OER. It was synthesized on Ni foam by hydrothermal treatment followed by

phosphorization at 400 °C for 2 h under an Ar atmosphere. P-CoMoO<sub>4</sub> exhibits higher activity, higher electrochemical surface area, and lower charge transfer resistance for the HER and OER than CoMoO<sub>4</sub>. It is composed of phosphorus-doped monoclinic  $\beta$ -CoMoO<sub>4</sub>. It has low crystallinity. It contains Co, Mo, O, and P, which are homogeneously distributed. In the high-resolution XPS spectra, the Co 2p peak of P-CoMoO<sub>4</sub> exhibits a slight positive shift, when compared to that of CoMoO<sub>4</sub>, suggesting a modified electronic structure due to the phosphorus doping. It contains Mo <sup>$\delta^+$</sup>  ( $2 < \delta < 4$ ), Mo<sup>4+</sup>, Mo<sup>5+</sup>, and Mo<sup>6+</sup>, whereas CoMoO<sub>4</sub> without P doping contains only Mo<sup>6+</sup>. It contains PO<sub>4</sub><sup>3-</sup>. It contains oxygen vacancies. It possesses micro-rod array morphology. It undergoes surface reconstruction during the HER and OER. It is reconstructed into Co(OH)<sub>2</sub>-CoMoO<sub>4</sub>/P-CoMoO<sub>4</sub> during the HER, while it is converted into CoOOH/P-CoMoO<sub>4</sub> during the OER. For the HER in 1 M KOH, it affords an  $\eta$  of  $-44$  mV at  $-10$  mA cm<sup>-2</sup>, suggesting its very high activity, while it undergoes negligible decay at  $-50$  mA cm<sup>-2</sup> for 100 h, suggesting its very high stability. For overall water splitting in 1 M KOH, P-CoMoO<sub>4</sub>//P-CoMoO<sub>4</sub> affords a potential of 1.54 V at 10 mA cm<sup>-2</sup>, suggesting its very high activity.

Fabricating an electrocatalyst on a 3D periodic porous electrode could facilitate the evolution of gas bubbles, reduce bubble coalescence, expose abundant active sites, and that could enhance the activity for the HER and OER even at high current densities. Kou *et al.*<sup>16</sup> reported that the C-Ni<sub>1-x</sub>O/3D printed Ni exhibits very high activity and stability for the HER and OER in 1 M KOH. It was prepared by 3D printing with solvent evaporation followed by heat treatment followed by coating of the catalyst (Fig. 1): at first, a Ni lattice structure was obtained through a direct ink writing technique, where the paste-like ink was composed of Ni particles, poly(lactic-co-glycolic acid) (PLGA), dichloromethane (DCM), and ethylene glycol butyl ether (EGBE). Then, the printed parts were subjected to drying in air followed by thermal treatment (300 °C for 1 h and then 600 °C for 1 h in an H<sub>2</sub> atmosphere) followed by heat treatment (900 °C in an Ar atmosphere for 3 h). Later, nickel oxalate was grown on 3D printed Ni (working electrode) by applying 50 V for 10 minutes in 0.3 M oxalic acid as the electrolyte, where Ni foil was used as a counter electrode. Finally, C-Ni<sub>1-x</sub>O/3D printed Ni was obtained by heating the nickel oxalate/3D printed Ni at 400 °C for 40 minutes in the Ar atmosphere. C-Ni<sub>1-x</sub>O/3D printed Ni exhibits higher activity and electrochemical surface area for the HER and OER than C-Ni<sub>1-x</sub>O/Ni foam. C-Ni<sub>1-x</sub>O on 3D printed Ni with a periodic porous structure exhibits much higher bubble flow and much less bubble coalescence than C-Ni<sub>1-x</sub>O on 3D Ni foam with a disordered porous structure. It is composed of 3D printed Ni having periodic pore structures, which is decorated by carbon doped nickel oxide, where the 3D porous structure could facilitate the evolution of gas bubbles, diminish bubble coalescence, and expose abundant active sites, which could enhance the activity for the HER and OER even at large current densities. The C-Ni<sub>1-x</sub>O/3D printed Ni affords an  $\eta$  of  $-245$  mV at a current





**Fig. 1** (a) Schematic diagram depicting the ink formulation process; the graph located in the upper part of (b) represents the elastic modulus versus shear stress, and the graph located in the lower part of (b) indicates the shear stress versus shear rate for Ni-based inks with solid loadings of 50 vol% (red color) and 40 vol% (blue color); (c)–(e) schematic pictures depicting the fabrication process of C-Ni<sub>1-x</sub>O/3D printed Ni, where the inset in (d) shows its corresponding digital photographic image; (f) and (g) SEM images of C-Ni<sub>1-x</sub>O/3D printed Ni; LSV curves of C-Ni<sub>1-x</sub>O/3D printed Ni in comparison with C-Ni<sub>1-x</sub>O/Ni foam for (h) the HER and (i) OER in 1 M KOH (reproduced with permission from ref. 16 Copyright 2020, Wiley-VCH GmbH).

density of  $-1000 \text{ mA cm}^{-2}$  for the HER (Fig. 1h), while it affords an  $\eta$  of 425 mV at a current density of  $1000 \text{ mA cm}^{-2}$  for the OER (Fig. 1i) in 1 M KOH, showing significantly high activity.

Integrating N-doped carbon with nanostructured transition metal/metal oxide could redistribute intermediates, enhance the conductivity, facilitate the evolution of gas, and expose abundant active sites, and that could enhance the performance of the HER and OER. Qian *et al.*<sup>15</sup> observed that Ni/MoO<sub>2</sub>@CN exhibits significantly very high activity and stability for the HER and OER. It was prepared on Ni foam by hydrothermal treatment followed by carbonization at 450 °C for 2 h under a H<sub>2</sub>/Ar atmosphere. Ni/MoO<sub>2</sub>@CN exhibits higher activity for the HER

than MoO<sub>2</sub>@CN, while it exhibits higher activity for the OER than Ni/MoO<sub>2</sub>. It is composed of Ni/MoO<sub>2</sub>, which is encapsulated by N-doped carbon. It exhibits a three-phase heterojunction. It contains Ni, Mo, C, N, and O, which are homogeneously distributed. In the high-resolution XPS spectra, the Ni 2p peak of Ni/MoO<sub>2</sub>@CN exhibits a slight positive shift, and the Mo 3d peak of Ni/MoO<sub>2</sub>@CN exhibits a slight negative shift, when compared to that of Ni/MoO<sub>2</sub>, suggesting a modified electronic structure due to the N doped carbon. It possesses nano-needle morphology. DFT calculations disclose the redistribution of electrons at the triple-phase heterojunction interface, which could provide optimal adsorption energy with



intermediates, and could enhance the performance of the HER and OER. For the OER in 1 M KOH, it affords an  $\eta$  of 250 mV at 10 mA cm<sup>-2</sup>, and an  $\eta$  of 420 mV at a current density of 1000 mA cm<sup>-2</sup>, suggesting its significantly very high activity, while it undergoes negligible decay at a current density of 1000 mA cm<sup>-2</sup> for 200 h, suggesting its significantly very high stability. For the HER in 1 M KOH, it affords an  $\eta$  of -33 mV at -10 mA cm<sup>-2</sup>, and an  $\eta$  of -267 mV at a current density of -1000 mA cm<sup>-2</sup>, suggesting its significantly very high activity, while it undergoes negligible decay at a current density of -1000 mA cm<sup>-2</sup> for 200 h, suggesting its significantly very high stability. For overall water splitting in 1 M KOH, Ni/MoO<sub>2</sub>@CN//Ni/MoO<sub>2</sub>@CN affords a potential of 1.83 V at 200 mA cm<sup>-2</sup>, and a potential of 2.02 V at a current density of 1000 mA cm<sup>-2</sup>, suggesting its significantly very high activity, while it affords 98.19% retention at 1.7 V for 168 h, suggesting its significantly very high stability.

The utilization of waste as a source for the green synthesis of electrocatalysts is highly desirable, whereas per-fluorooctanoic acid, an aqueous pollutant, can be used as a fluorine source. Lu *et al.*<sup>27</sup> observed that WO<sub>3</sub>@F<sub>0.1</sub>-C exhibits enhanced activity and stability for the OER. It was obtained by the plasma-induced assembly method, where per-fluorooctanoic acid (a pollutant) is used as an F source. WO<sub>3</sub>@F<sub>0.1</sub>-C exhibits higher activity, higher electrochemical surface area, and lower charge transfer resistance for the OER than WO<sub>3</sub>@C. It is composed of ultra-small WO<sub>3</sub> nanoparticles (monoclinic crystals), which are decorated on F-doped graphite sheets. It exhibits an  $I_D/I_G$  ratio of 0.924, suggesting the existence of high defects and low graphitization degree. In the high-resolution XPS spectra, the W 4f peak of WO<sub>3</sub>@F<sub>0.1</sub>-C exhibits a slight shift, when compared to that of WO<sub>3</sub>@C, suggesting a modified electronic structure due to the F doping. The DFT calculations disclose that the energy barrier for OH deprotonation is lowered by the F-doping, and the hydroxyl adsorption is enhanced by WO<sub>3</sub>.

The fabrication of semi-oxidized transition metal oxide nanoparticles anchored on carbon produces highly active defective metal (oxy)hydroxides during the OER, and that could enhance the performance of the OER. Wang *et al.*<sup>41</sup> observed that Co-CoO/GO (graphene oxide) exhibits enhanced activity and stability for the OER. It was synthesized by sonication for 1 h followed by hydrothermal treatment followed by annealing at 450 °C for 30 min under an Ar atmosphere. Co-CoO/GO exhibits higher activity and lower charge transfer resistance for the OER than Co/GO, and Co<sub>3</sub>O<sub>4</sub>/GO. It contains metallic Co, crystalline CoO, and graphene oxide. It contains Co, C, and O, which are homogeneously distributed. It exhibits the formation of defective CoOOH during the OER.

Constructing Mott-Schottky heterojunctions could lead to the spontaneous flow of electrons at the metal-semiconductor heterointerfaces till the work functions reach equilibrium on both sides, and that could modify the electronic structure,

provide optimal adsorption energy with intermediates, enhance the conductivity, and that could enhance the performance for the HER and OER. Li *et al.*<sup>42</sup> observed that Ni/CeO<sub>2</sub>@N-CNFs exhibit enhanced activity and stability for the HER and OER (CNFs: carbon nanofibers). They were synthesized by electro-spinning followed by stabilization at 250 °C for 2 h followed by carbonization at 600 °C for 3 h under an N<sub>2</sub> atmosphere. The Ni/CeO<sub>2</sub>@N-CNFs exhibits higher activity and electrochemical surface area for the HER and OER than Ni@N-CNFs and CeO<sub>2</sub>@N-CNFs. It is composed of crystalline Ni/CeO<sub>2</sub> nanoparticles, which are encased into N-doped carbon nanofibers. It exhibits a heterointerface between Ni and CeO<sub>2</sub>. It contains Ce, Ni, O, and N, which are homogeneously distributed. In the high-resolution XPS spectra, the Ce 3d peak of Ni/CeO<sub>2</sub>@N-CNFs exhibits a slight negative shift, when compared to that of CeO<sub>2</sub>@N-CNFs, while the Ni 2p peak of Ni/CeO<sub>2</sub>@N-CNFs exhibits a slight positive shift, when compared to that of Ni@N-CNFs, suggesting a modified electronic structure possibly due to the partial transfer of electrons from Ni to CeO<sub>2</sub> at the heterointerface in Ni/CeO<sub>2</sub>@N-CNFs. It contains oxygen vacancies. It is porous. For overall water splitting in 1 M KOH, the Ni/CeO<sub>2</sub>@N-CNFs//Ni/CeO<sub>2</sub>@N-CNFs affords a potential of 1.56 V at 10 mA cm<sup>-2</sup>, suggesting its very high activity, while it undergoes negligible decay for 100 h, suggesting its very high stability.

**2.1.2. Constructing hydroxide electrocatalysts.** Annealing at a moderate temperature on electrodeposited transition metal hydroxides could enhance the conductivity by removing a part of the intercalated water to achieve high performance for the OER. Tao *et al.*<sup>43</sup> observed that the annealed  $\alpha$ -Ni(OH)<sub>2</sub> exhibits enhanced activity and stability for the OER. It was prepared on etched Ti foil by electrodeposition followed by annealing at 150 °C for 1 h under an air atmosphere. The annealed  $\alpha$ -Ni(OH)<sub>2</sub> exhibits higher activity and lower charge transfer resistance for the OER than as-deposited Ni(OH)<sub>2</sub>, suggesting the enhanced performance on annealed  $\alpha$ -Ni(OH)<sub>2</sub> due to the improved conductivity. The annealing treatment leads to the removal of a fraction of the intercalated water in the as-deposited  $\alpha$ -Ni(OH)<sub>2</sub>, causing enhanced conductivity and activity for the OER. Moreover, it exhibits the formation of highly active  $\gamma$ -Ni<sup>2.63</sup>O<sub>0.63</sub>(OH)<sub>1.37</sub> during the OER.

Reduction and oxidation can occur by applying pulsed potentials on the substrate in the electrochemical method; while utilizing this strategy, a scalable, ultrafast, and energy-efficient synthesis route can be achieved for the fabrication of highly active electrocatalysts at ambient temperature, which is highly desirable for green synthesis. Liu *et al.*<sup>26</sup> observed that the IronCE10s exhibit enhanced activity and stability for the OER, while it was prepared on the cheap iron substrate by applying pulsed potentials for 10 s (+2.4 V for 5 s followed by -2.4 V for 5 s) in NiSO<sub>4</sub> electrolyte at 25 ± 1 °C, where the substrate was used as a counter electrode. The IronCE10s exhibits higher activity for the OER than



IronWE10s, IronCE5s, IronCE60s, and IronCE360s. It contains Ni, Fe, and O, while it may be iron-doped amorphous nickel hydroxide. The morphology of the prepared samples was a nanosheet array.

The effect of the substrate in the electrodeposition process could alter the conductivity and electrochemical surface area of the electrocatalyst, and that could influence the performance of the OER. Yin *et al.*<sup>44</sup> observed that FeNiOH on Ni foil exhibits enhanced activity and stability for the OER. It was obtained on the cleaned Ni foil by the electrodeposition method at 20 °C for 600 s. FeNiOH on Ni foil exhibits higher activity, higher electrochemical surface area, and lower charge transfer resistance for the OER than FeNiOH on Fe foil. It is an amorphous FeNi hydroxide, which is distributed homogeneously. It possesses nanostructured morphology. For the OER in 1 M KOH, it affords an  $\eta$  of 200 mV at 10 mA cm<sup>-2</sup>, suggesting its very high activity, while it undergoes negligible decay at 90 mA cm<sup>-2</sup> after 1000 cycles of CV, suggesting its high durability.

Fabrication of transition bimetallic hydroxides through a facile synthesis route at ambient temperature could enhance the performance of the OER. Zhuo *et al.*<sup>45</sup> demonstrated a rapid, facile, cost-effective, and scalable (area: 2000 cm<sup>2</sup>) synthesis route at room temperature for Ni(Fe)(OH)<sub>2</sub>, where it was synthesized by submerging the pre-cleaned Ni foam for 60 s in 0.2 M Fe(NO<sub>3</sub>)<sub>3</sub> at ambient temperature, while it exhibits high activity and stability for the OER. The incorporation of Fe in Ni hydroxide and the *in situ* formation of Ni(Fe)OOH from Ni(Fe)(OH)<sub>2</sub> during electrolysis are attributed to the enhancement in the performance for the OER. For the OER in 1 M KOH, it affords an  $\eta$  of 240 mV at 10 mA cm<sup>-2</sup>, and an  $\eta$  of 680 mV at a current density of 1000 mA cm<sup>-2</sup>, suggesting its significantly high activity, while it affords high stability.

Metal-organic frameworks (MOFs) can be converted into hydroxides/(oxy)hydroxides with abundant oxygen vacancies and mesopores using an alkaline hydrolysis-oxidation strategy with the assistance of an electric field, and that could modify the electronic structure, afford optimal adsorption energy with intermediates, enhance the electrochemical surface area, and that could enhance the performance for the OER. Li *et al.*<sup>46</sup> observed that CoNiFe-OH exhibits enhanced activity and stability for the OER. It was synthesized by the following steps. At first, Co/Ni/Fe MOFs were obtained on Ni foam by hydrothermal treatment. Finally, CoNiFe-OH was obtained using an alkaline hydrolysis-oxidation strategy with the assistance of an electric field (at 1.45 V for 30 min), where Co/Ni/Fe MOFs were used as the working electrode, and 1 M KOH was used as the electrolyte. The CoNiFe-OH exhibits higher activity and electrochemical surface area for the OER than CoNiFe-H. It is polycrystalline, containing Co(OH)<sub>2</sub>, CoOOH, Ni(OH)<sub>2</sub>, NiOOH, and FeOOH phases. It contains Fe, Co, Ni, and O, which are homogeneously distributed. It contains oxygen vacancies. It possesses nanostructured ultrathin hexagonal plate-like morphology. It is mesoporous. For the OER in 1 M KOH, it affords an  $\eta$  of 207 mV at 10 mA cm<sup>-2</sup>, suggesting its very high activity.

Doping of cerium into NiFe hydroxide could increase the valence state of Fe, modify the electronic structure, and afford optimal adsorption energy with intermediates, and that could enhance the performance of the OER. Liu *et al.*<sup>47</sup> observed that Ce-NiFe exhibits enhanced activity and stability for the OER. It was prepared on NiFe foam by the electrodeposition method. Ce-NiFe exhibits higher activity and electrochemical surface area for the OER than NiFe, CeNi, and CeFe. It is an amorphous Ce-doped NiFe hydroxide. It contains Ce, Ni, Fe, and O, which are homogeneously distributed. In the high-resolution XPS spectra, the Ni 2p and Fe 2p peaks of Ce-NiFe exhibit a slight positive shift, when compared to that of NiFe, suggesting a modified electronic structure. It contains high valence Fe ions (Fe > 3+). For the OER in 1 M KOH, it affords an  $\eta$  of 195 mV at 10 mA cm<sup>-2</sup>, and an  $\eta$  of ~770 mV at a current density of 1000 mA cm<sup>-2</sup>, suggesting its very high activity, while it affords reasonable stability at a current density of 1000 mA cm<sup>-2</sup> for 100 h, suggesting its very high stability.

Fabrication of nanostructured transition bimetallic carbonate hydroxides could modify the electronic structure, afford optimal adsorption energy with intermediates, facilitate the evolution of gas, and expose abundant active sites, and that could boost the performance for the HER and OER. Hui *et al.*<sup>17</sup> observed that Fe-Co-CO<sub>3</sub>-OH exhibits significantly very high activity and stability for the HER and OER. It was obtained on Ni foam by the hydrothermal treatment. Fe-Co-CO<sub>3</sub>-OH exhibits higher activity for the HER and OER than Co-CO<sub>3</sub>-OH and Fe-CO<sub>3</sub>-OH. It is Fe-doped Co carbonate hydroxide. It is crystalline. It exhibits a homogeneous distribution of Fe and Co. In the high-resolution XPS spectra, the Co 2p peak of Fe-Co-CO<sub>3</sub>-OH exhibits a slight shift, when compared to Co-CO<sub>3</sub>-OH, suggesting a modified electronic structure due to the Fe doping. It possesses nanosheet array morphology. For the OER in 1 M KOH, it affords an  $\eta$  of 228 mV at 10 mA cm<sup>-2</sup>, and an  $\eta$  of 308 mV at a current density of 1000 mA cm<sup>-2</sup>, suggesting its substantially very high activity. For the HER in 1 M KOH, it affords an  $\eta$  of -77 mV at -10 mA cm<sup>-2</sup>, and an  $\eta$  of -256 mV at a current density of -1000 mA cm<sup>-2</sup>, suggesting its substantially very high activity, while it undergoes negligible decay at a current density of -1000 mA cm<sup>-2</sup> after 10 000 cycles of CV, suggesting its substantially very high durability. Moreover, Tang *et al.*<sup>48</sup> observed that Co-Mn-CO<sub>3</sub>-OH exhibits enhanced activity and stability for the HER and OER. It was obtained on Ni foam by hydrothermal treatment. Co-Mn-CO<sub>3</sub>-OH exhibits higher activity and electrochemical surface area for the HER and OER than Co-CO<sub>3</sub>-OH and MnCO<sub>3</sub>. It is Mn-doped Co carbonate hydroxide. It has low crystallinity. It contains Mn, Co, C, and O, which are homogeneously distributed. The number of electrons present in the 3d orbital of the Co atom in Co-Mn-CO<sub>3</sub>-OH is about 7.30, which is higher than that of Co-CO<sub>3</sub>-OH, suggesting the modified electronic structure possibly due to the partial transfer of electrons from Mn to Co. It possesses nanosheet array morphology. For the OER in 1 M KOH, it affords an  $\eta$  of 462 mV



at a current density of  $1000 \text{ mA cm}^{-2}$ , suggesting its very high activity.

### 2.1.3. Constructing (oxy)hydroxide electrocatalysts.

Creating abundant defects in Fe (oxy)hydroxide could generate highly active species after electrochemical activation, and enhance the conductivity, and performance of the OER. Hu *et al.*<sup>49</sup> observed that the Defect-FeOOH activated exhibits enhanced activity and stability for the OER. It was obtained by a solvothermal treatment followed by electron beam irradiation followed by electrochemical activation. The Defect-FeOOH activated exhibits higher activity and lower charge transfer resistance for the OER than FeOOH activated. The Defect-FeOOH is composed of the  $\beta$ -FeOOH phase with abundant defects (without oxygen vacancies), while it contains a mixed phase ( $\alpha$ -FeOOH and  $\beta$ -FeOOH) after electrochemical activation. It contains high valence Fe ions ( $\text{Fe}^{3.13+}$ ). It possesses nanorod morphology.

Doping sulfur in Fe (oxy)hydroxide could activate the redox reactivities of the lattice oxygen and Fe, and that could enhance the performance of the OER. Therefore, fabricating sulfur-doped Fe (oxy)hydroxide at ambient temperature through a facile, scalable, energy-efficient, and ultrafast synthesis route is highly desirable for green synthesis. Chen *et al.*<sup>24</sup> observed that S-FeOOH exhibits enhanced activity and stability for the OER. It was obtained by immersing the cleaned Fe foam for 20 min at room temperature in the solution containing  $\text{Fe}(\text{NO}_3)_3$  and  $\text{Na}_2\text{S}_2\text{O}_3$ . S-FeOOH exhibits higher activity and electrochemical surface area for the OER than FeOOH. It is polycrystalline, containing S-doped  $\beta$ -FeOOH. It exhibits a homogeneous distribution of S. In the high-resolution XPS spectra, the Fe 2p peak of S-FeOOH slightly shifts, when compared to that of FeOOH, suggesting a modified electronic structure due to the S doping. It contains oxygen vacancies. The redox reactivities of the lattice oxygen and Fe in FeOOH are activated due to S doping. It possesses nanosheet array morphology. For the OER in 1 M KOH, it affords an  $\eta$  of 244 mV at  $10 \text{ mA cm}^{-2}$ , suggesting its very high activity, while it exhibits negligible decay at  $20 \text{ mA cm}^{-2}$  for 100 h, suggesting its very high stability.

The role of cations in the electrolyte could influence the activity of the OER. Hou *et al.*<sup>50</sup> observed that the activity of the NiFe-(OOH)-based catalyst for the OER in different electrolytes is in the following order:  $\text{CsOH} > \text{KOH} > \text{NaOH} > \text{LiOH}$ . The catalytic activity trend is nearly associated with the potential for maximum entropy of the system. The catalytic activity has been nearly related to the variable length of Ni–O bonds in the NiOOH active phase structure.

Fabrication of transition bimetallic alloy/(oxy) hydroxide heterostructures could tune the electronic structure, afford optimal adsorption energy with intermediates, expose abundant active sites, improve charge/mass transfer, facilitate gas evolution, and that could improve the performance for the HER and OER. Lv *et al.*<sup>11</sup> observed that c-NiFe/a-NiFeOOH@NiMo (c: crystalline; a: amorphous) exhibits enhanced activity and

stability for the HER and OER. It was obtained on carbon fiber cloth by galvanostatic electrodeposition at  $\sim 0^\circ\text{C}$  followed by cyclic voltammetry treatment followed by potentiostatic electrodeposition. c-NiFe/a-NiFeOOH@NiMo exhibits higher activity and lower charge transfer resistance for the HER and OER than c-NiFe/a-NiFeOOH and NiMo. It contains hetero-junctions. It exhibits a core-shell structure, containing NiMo particles as the core, and thin c-NiFe/a-NiFeOOH nanosheets as the shell, where the thin nanosheet is composed of crystalline NiFe nanoflowers (cubic  $\text{Ni}_{0.36}\text{Fe}_{0.64}$  alloy), which are embedded in amorphous NiFeOOH. a-NiFeOOH contains nanosized pores. The ultrafine NiFe alloy nanocrystals possesses abundant edges and high electronic conductivity, and the amorphous NiFeOOH support possesses abundant defects and nanosized pores, while the NiMo alloy can afford firm grasp to the c-NiFe/a-NiFeOOH nanosheets, and that could modify the electronic structure, provide optimal adsorption energy with intermediates, expose abundant active sites, enhance charge/mass transfer, facilitate gas evolution, which could enhance the performance for the HER and OER. For the OER in 1 M KOH, c-NiFe/a-NiFeOOH@NiMo affords 133.2 mV at  $20 \text{ mA cm}^{-2}$ , suggesting its very high activity. For the HER in 1 M KOH, it affords an  $\eta$  of  $-91.9 \text{ mV}$  at  $-20 \text{ mA cm}^{-2}$ , suggesting its very high activity. For overall water splitting in 1 M KOH, c-NiFe/a-NiFeOOH@NiMo//c-NiFe/a-NiFeOOH@NiMo affords a potential of 1.45 V at  $10 \text{ mA cm}^{-2}$ , suggesting its very high activity, while it affords 95.86% retention at  $100 \text{ mA cm}^{-2}$  for 100 h, suggesting its very high stability.

The fabrication of NiFe-based electrocatalysts for the OER through an electrodeposition process using a deep eutectic solvent (DES) with Ni as a source in the form of nitrate could form multi vacancies upon electrolysis, and that could enhance the performance for the OER. Wei *et al.*<sup>6a</sup> fabricated NiFe based electrocatalysts for the OER through a one-step electrodeposition process, where Fe was used as a sacrificial anode and ethaline-based DES with nickel nitrate was used as an electrolyte. The utilization of nitrate ions in the electrodeposition process for the preparation of NiFe based catalysts could generate multiple vacancies (such as O, Ni, and Fe vacancies) during water oxidation, leading to optimal adsorption energies with intermediates, and that could boost the performance for the OER. For the OER in 1 M KOH, it affords an  $\eta$  of 256 mV at  $10 \text{ mA cm}^{-2}$ , suggesting its high activity.

**2.1.4. Fabricating layered double hydroxide (LDH) electrocatalysts.** Fabrication of highly active transition bimetallic LDH as an electrocatalyst at ambient temperature through a facile energy-efficient synthesis route is highly desirable for green synthesis. Zhao *et al.*<sup>25</sup> observed that the NiFe LDH exhibits enhanced activity and stability for the OER. It was prepared by immersing cleaned, acid-treated Fe foam in  $\text{NiSO}_4$  solution under ambient conditions. It is composed of four layers, an Fe foam substrate at the bottom, nanoparticle aggregates on the substrate, an interfacial film, and nanosheets at the top. It is NiFe LDH with a rhombohedral structure. It



contains Ni, Fe, and O, which are homogeneously distributed. It affords reasonable stability at  $100 \text{ mA cm}^{-2}$  for 192 h, suggesting its very high stability.

The electrochemical activation of transition bimetallic LDH can reconstruct the surface, which could generate highly active sites, enhance the surface area, and that could improve the performance of the HER and OER. Pehlivan *et al.*<sup>51</sup> observed that the NiFe LDH activated exhibits enhanced activity for the HER and OER. Crystalline NiFe LDH was synthesized on pretreated Ni foam by hydrothermal treatment. NiFe LDH activated affords an  $\eta$  of 201 mV at  $10 \text{ mA cm}^{-2}$  for the OER, and it affords an  $\eta$  of  $-189 \text{ mV}$  at  $-10 \text{ mA cm}^{-2}$  for the HER in 1 M KOH, suggesting its very high activity.

Transition bimetallic catalysts having a structure almost similar to the NiFe LDH can be fabricated by the spray pyrolysis deposition technique, and that could enhance the activity and stability of the OER. An *et al.*<sup>52</sup> observed that the NiFe-based catalyst exhibits enhanced activity and stability for the OER. It was obtained on a fluorine-doped tin oxide glass substrate by an ultrasonic spray pyrolysis deposition method. The NiFe-based catalyst aged at 0 min exhibits higher activity and lower charge transfer resistance for the OER than the NiFe-based catalyst aged at 2, 4, and 8 min. It is composed of NiFe oxide and layered hydroxyl nitrate. The structure of the NiFe-based catalyst is almost similar to the that of the typical NiFe LDH. It contains Fe, Ni, O, and N with a film thickness of 100 nm and uniform coral-like stripes.

Fabrication of heterostructured metal (oxy)hydroxide/transition bimetallic LDH through a facile one-step synthesis route is highly desirable. Li *et al.*<sup>53</sup> observed that the FeOOH@NiFe LDH exhibits enhanced activity and stability for the OER. It was synthesized by immersing the cleaned Ni foam in FeCl<sub>3</sub> solution at 100 °C for 5 s. FeOOH@NiFe LDH exhibits higher activity, higher electrochemical surface area, and lower charge transfer resistance for the OER than FeOOH and NiFe LDH. It is crystalline, containing  $\beta$ -FeOOH and NiFe LDH phases. It exhibits a heterointerface. It contains Fe, Ni, and O, which are uniformly distributed. It possesses nanosheet array morphology. During the OER, it is converted into highly active FeOOH@ $\beta$ -Ni(Fe)OOH phases. For the OER in 1 M KOH, it affords an  $\eta$  of 210 mV at  $10 \text{ mA cm}^{-2}$ , suggesting its very high activity, while it undergoes negligible decay for 100 h, suggesting its very high stability.

Negatively charged metal nanoparticles can be integrated with positively charged transition bimetallic LDH due to the electrostatic attraction by the physical blending method, which could modify the electronic structure, and that could enhance the performance of the OER. Wu *et al.*<sup>54</sup> observed that the Ag@NiFe LDH exhibits enhanced activity and stability for the OER. It was prepared by the physical blending method, where Ag@NiFe LDH can be precipitated when adding Ag with NiFe LDH due to the electrostatic attraction between positively charged NiFe LDH and negatively charged Ag nanoparticles, while the NiFe LDH was prepared by hydrothermal treatment.

Ag@NiFe LDH exhibits higher activity, higher electrochemical surface area, and lower charge transfer resistance for the OER than Au@NiFe LDH and NiFe LDH. It is crystalline. It is composed of metallic Ag nanoparticles, which are anchored on NiFe LDH nanosheets. It exhibits a heterointerface. In the high-resolution XPS spectra, the Ni 2p and Fe 2p peaks of Ag@NiFe LDH exhibit a slight positive shift, when compared to that of NiFe LDH, while the Ag 3d peaks of Ag@NiFe LDH exhibit a slight negative shift, when compared to that of metallic Ag, suggesting a modified electronic structure possibly due to the partial transfer of electrons from NiFe LDH to Ag.

Doping of cerium into transition bimetallic LDH could modify the electronic structure, and that could enhance the performance of the HER and OER. Dhandapani *et al.*<sup>55</sup> observed that the Ce@NiCo LDH exhibits enhanced activity and stability for the HER and OER. It was obtained on cleaned Ni foam by hydrothermal treatment. Ce@NiCo LDH exhibits higher activity and lower charge transfer resistance for the HER and OER than NiCo LDH. It is 25.5% Ce doped NiCo LDH. It contains Ce, Ni, Co, and O, which are homogeneously distributed. In the high-resolution XPS spectra, the Co 2p peak of Ce@NiCo LDH exhibits a slight shift compared to that of NiCo LDH, suggesting a modified electronic structure. It possesses nano petal morphology.

Heterostructured transition bimetallic phosphide/bimetallic LDH can be obtained by the partial phosphidation of bimetallic LDH, and that could modify the electronic structure, afford optimal adsorption energy with intermediates, which could enhance the activity and stability for the HER and OER. Zheng *et al.*<sup>56</sup> observed that the c-CoFeP/a-CoFe LDH exhibits enhanced activity and stability for the OER, whereas the c-CoMnP/a-CoMn LDH (c: crystalline; a: amorphous) exhibits enhanced activity and stability for the HER. The c-CoFeP/a-CoFe LDH or c-CoMnP/a-CoMn LDH was prepared on pretreated Ni foam by hydrothermal treatment followed by partial phosphidation for 2 h at 250 °C under an Ar atmosphere. The c-CoFeP/a-CoFe LDH exhibits higher activity and electrochemical surface area for the OER than c-CoMnP/a-CoMn LDH, c-CoNiP/a-CoNi LDH, c-CoCuP/a-CoCu LDH, and c-CoZnP/a-CoZn LDH. The c-CoMnP/a-CoMn LDH exhibits higher activity and electrochemical surface area for the HER than c-CoFeP/a-CoFe LDH, c-CoNiP/a-CoNi LDH, c-CoCuP/a-CoCu LDH, and c-CoZnP/a-CoZn LDH. The c-CoFeP/a-CoFe LDH is the crystalline CoFeP decorated amorphous CoFe LDH heterostructure. It possesses a nanostructure. The c-CoMnP/a-CoMn LDH is the crystalline CoMnP decorated amorphous CoMn LDH heterostructure. It possesses a nanostructure. For overall water splitting in 1 M KOH, the c-CoFeP/a-CoFe LDH<sup>OER</sup>//c-CoMnP/a-CoMn LDH<sup>HER</sup> affords a potential of 1.498 V at  $10 \text{ mA cm}^{-2}$ , confirming its very high activity.

Integrating LDH with MXene could modify the electronic structure and provide optimal adsorption energy with intermediates, enhancing the activity and stability of the HER and OER. Yu *et al.*<sup>57</sup> observed that the NiFeLa LDH/v-MXene



(vertically aligned MXene) exhibits significantly very high activity and stability for the HER and OER. It was synthesized *via* the following steps: at first,  $\text{Ti}_3\text{C}_2$  MXene nanosheets were prepared by selectively etching Al layers in  $\text{Ti}_3\text{AlC}_2$ . Then, vertically aligned  $\text{Ti}_3\text{C}_2$  MXene was obtained on Ni foam by electrophoretic deposition followed by freeze-drying. Finally, NiFeLa LDH/*v*-MXene was obtained by electrodeposition. The NiFeLa LDH/*v*-MXene exhibits higher activity for the HER and OER than NiFe-LDH/*v*-MXene, NiFeLa LDH/MXene, NiFeLa LDH, and *v*-MXene. It comprises amorphous NiFeLa LDH nanosheets on crystalline  $\text{Ti}_3\text{C}_2$  MXene nanosheets, where the MXene is vertically aligned on Ni foam. It contains Ti, C, Ni, Fe, La, and O, which are homogeneously distributed. In the high-resolution XPS spectra, the Ni 2p peak of NiFeLa LDH/*v*-MXene exhibits a slight positive shift compared to that of NiFe LDH/*v*-MXene, suggesting a modified electronic structure. It exhibits super hydrophilicity with a contact angle of  $0^\circ$ . For the OER in 1 M KOH, it affords an  $\eta$  of 191 mV at  $10 \text{ mA cm}^{-2}$ , suggesting its very high activity. In contrast, it undergoes negligible decay at  $100 \text{ mA cm}^{-2}$  for 1200 h, suggesting its robust stability. For the HER in 1 M KOH, it affords an  $\eta$  of  $-38 \text{ mV}$  at  $-10 \text{ mA cm}^{-2}$ , suggesting its very high activity, while it affords reasonable stability at  $-100 \text{ mA cm}^{-2}$  for 400 h, suggesting its very high stability, and it undergoes negligible decay at  $-700 \text{ mA cm}^{-2}$  after 2000 cycles of CV, suggesting its high durability. For overall water splitting in 1 M KOH, the NiFeLa LDH/*v*-MXene//NiFeLa LDH/*v*-MXene affords a potential of 1.48 V at  $10 \text{ mA cm}^{-2}$ , suggesting its very high activity, while it undergoes negligible decay at  $100 \text{ mA cm}^{-2}$  for 400 h, suggesting its robust stability.

## 2.2. Fabricating chalcogenide (sulfide and selenide) electrocatalysts

### 2.2.1. Fabricating sulfide electrocatalysts.

Doping cobalt in nickel sulfide could modify the electronic structure, boosting the performance of the HER and OER. Li *et al.*<sup>58</sup> observed that Co- $\text{Ni}_3\text{S}_2$  exhibits enhanced activity and stability for the HER and OER. It was prepared on cleaned Ni mesh by electrodeposition followed by hydrothermal sulfurization. It is Co-doped rhombohedral  $\text{Ni}_3\text{S}_2$ . It contains Ni, Co, and S, which are homogeneously distributed. In the high-resolution XPS spectra, the Ni 2p peak of Co- $\text{Ni}_3\text{S}_2$  exhibits a slight shift when compared to that of  $\text{Ni}_3\text{S}_2$ , suggesting a modified electronic structure due to Co doping. It possesses a leaf-like morphology.

Fabrication of cobalt-doped nickel sulfide having an ultrathin nanostructure could modify the electronic structure and facilitate the evolution of gas even at high current densities, boosting the performance of the HER and OER. Jian *et al.*<sup>59</sup> observed that Co- $\text{Ni}_3\text{S}_2$  having an ultrathin nanosheet structure exhibits enhanced activity and stability for the HER and OER even at a current density of  $1000 \text{ mA cm}^{-2}$ , while it was obtained on pretreated Ni foam by a one-step hydrothermal treatment. Co- $\text{Ni}_3\text{S}_2$  exhibits higher activity for the HER and OER than  $\text{Ni}_3\text{S}_2$ . It is a Co-doped crystalline  $\text{Ni}_3\text{S}_2$ . It contains Ni, Co, and S, which are homogeneously distributed. It possesses an

ultrathin nanosheet structure. For the OER in 1 M KOH, it affords an  $\eta$  of 310 mV at  $50 \text{ mA cm}^{-2}$  and an  $\eta$  of 750 mV at a current density of  $1000 \text{ mA cm}^{-2}$ , suggesting its very high activity, while it undergoes negligible decay at a current density of  $1000 \text{ mA cm}^{-2}$  after 1000 cycles of CV, suggesting its high durability. For the HER in 1 M KOH, it affords an  $\eta$  of  $-220 \text{ mV}$  at  $-50 \text{ mA cm}^{-2}$  and an  $\eta$  of  $-850 \text{ mV}$  at a current density of  $-1000 \text{ mA cm}^{-2}$ , suggesting its very high activity, while it undergoes negligible decay at a current density of  $-1000 \text{ mA cm}^{-2}$  after 1000 cycles of CV, suggesting its high durability.

Besides, Jian *et al.*<sup>14</sup> observed that Sn- $\text{Ni}_3\text{S}_2$  exhibits substantially very high activity and stability for the HER and OER. It was synthesized on Ni foam by a one-step hydrothermal treatment. Sn- $\text{Ni}_3\text{S}_2$  exhibits higher activity for the HER and OER than  $\text{Ni}_3\text{S}_2$ , while it exhibits lower charge transfer resistance for the OER than  $\text{Ni}_3\text{S}_2$ . It is Sn-doped hexagonal  $\text{Ni}_3\text{S}_2$ . It contains Sn, Ni, and S, which are homogeneously distributed. It possesses an ultrathin nanosheet structure. For the OER in 1 M KOH, it affords an  $\eta$  of 267 mV at  $100 \text{ mA cm}^{-2}$  and an  $\eta$  of 580 mV at a current density of  $1000 \text{ mA cm}^{-2}$ , suggesting its significantly very high activity, while it undergoes negligible decay at a high current density of  $2000 \text{ mA cm}^{-2}$  after 10 000 cycles of CV, suggesting its substantially very high durability. For the HER in 1 M KOH, it affords an  $\eta$  of  $-171 \text{ mV}$  at  $-100 \text{ mA cm}^{-2}$  and an  $\eta$  of  $-570 \text{ mV}$  at a current density of  $-1000 \text{ mA cm}^{-2}$ , suggesting its significantly very high activity, while it undergoes negligible decay at a current density of  $-1000 \text{ mA cm}^{-2}$  after 10 000 cycles of CV, suggesting its significantly very high durability. For overall water splitting in 1 M KOH, Sn- $\text{Ni}_3\text{S}_2$ //Sn- $\text{Ni}_3\text{S}_2$  affords a potential of 1.46 V at  $10 \text{ mA cm}^{-2}$  and  $\sim 2.65 \text{ V}$  at a current density of  $1000 \text{ mA cm}^{-2}$ , suggesting its significantly very high activity.

Moreover, Mao *et al.*<sup>60</sup> observed that FeCo- $\text{Ni}_3\text{S}_4$  exhibits enhanced activity and stability for the OER. It was prepared on pretreated Ni foam by hydrothermal treatment followed by hydrothermal sulfurization. FeCo- $\text{Ni}_3\text{S}_4$  exhibits higher activity, higher electrochemical surface area, and lower charge transfer resistance for the OER than Fe- $\text{Ni}_3\text{S}_4$ , Co- $\text{Ni}_3\text{S}_4$ , and  $\text{Ni}_3\text{S}_4$ . It is Fe and Co dual-doped cubic  $\text{Ni}_3\text{S}_4$ . It contains Ni, S, Fe, and Co, which are homogeneously distributed. It exhibits a higher amount of high valence Ni ions ( $\text{Ni}^{3+}$ ) than  $\text{Ni}_3\text{S}_4$ . In the high-resolution XPS spectra, the Ni 2p peak of FeCo- $\text{Ni}_3\text{S}_4$  exhibits a slight shift when compared to that of  $\text{Ni}_3\text{S}_4$ , suggesting a modified electronic structure due to the Fe and Co dual doping. It possesses nanosheet array morphology. For the OER in 1 M KOH, it affords an  $\eta$  of 230 mV at  $20 \text{ mA cm}^{-2}$ , suggesting its very high activity, while it exhibits 22 mV decay at  $20 \text{ mA cm}^{-2}$  for 360 h, suggesting its very high stability, and it undergoes negligible decay at  $100 \text{ mA cm}^{-2}$  after 3000 cycles of CV, suggesting its very high durability.

Besides, Zhang *et al.*<sup>61</sup> reported that Fe, Ce- $\text{Ni}_x\text{S}_y$  exhibits enhanced activity and stability for the HER and OER. It was synthesized on the pretreated Ni foam by a one-step hydrothermal treatment. Fe, Ce- $\text{Ni}_x\text{S}_y$  exhibits higher activity and



electrochemical surface area for the OER than Fe-Ni<sub>x</sub>S<sub>y</sub>, Ce-Ni<sub>x</sub>S<sub>y</sub>, and Ni<sub>x</sub>S<sub>y</sub>. In comparison, it exhibits higher activity for the HER than Fe-Ni<sub>x</sub>S<sub>y</sub>, Ce-Ni<sub>x</sub>S<sub>y</sub>, and Ni<sub>x</sub>S<sub>y</sub>. It is Ce, Fe dual doped Ni<sub>x</sub>S<sub>y</sub>, where Ni<sub>x</sub>S<sub>y</sub> is crystalline, containing trigonal Ni<sub>3</sub>S<sub>2</sub> and orthorhombic Ni<sub>9</sub>S<sub>8</sub>. It contains Ni, Fe, Ce, and S, which are homogeneously distributed. In the high-resolution XPS spectra, the Ni 2p peak of Fe, Ce-Ni<sub>x</sub>S<sub>y</sub> exhibits a slight shift compared to that of Ni<sub>x</sub>S<sub>y</sub>, suggesting a modified electronic structure possibly due to the doping of Fe and Ce. It possesses nano forest array morphology.

Moreover, Huang *et al.*<sup>62</sup> observed that Fe-NiS-NiS<sub>2</sub> exhibits enhanced activity and stability for the HER and OER. It was prepared by co-precipitation followed by hydrothermal treatment followed by annealing at 350 °C for 2 h under an N<sub>2</sub> atmosphere. Fe-NiS-NiS<sub>2</sub> exhibits higher activity and electrochemical surface area for the HER and OER than Fe-NiS<sub>2</sub> and NiS-NiS<sub>2</sub>. It is Fe-doped crystalline NiS-NiS<sub>2</sub>. It exhibits the heterojunctions at a higher amount of high valence Ni ions (Ni<sup>3+</sup>) when compared to Fe-NiS<sub>2</sub>. In the high-resolution XPS spectra, the Ni 2p peak of Fe-NiS-NiS<sub>2</sub> exhibits a slight positive shift compared to that of Fe-NiS<sub>2</sub>, suggesting a modified electronic structure. It possesses a microsphere structure, where the microsphere is composed of nanoplates.

In addition, Fereja *et al.*<sup>63</sup> have observed that W-NiS<sub>2</sub>/MoO<sub>2</sub> exhibits enhanced activity for the HER and OER. It was obtained on cleaned carbon cloth by hydrothermal treatment followed by sulfurization at 400 °C for 2 h under an H<sub>2</sub>/Ar atmosphere. W-NiS<sub>2</sub>/MoO<sub>2</sub> exhibits higher activity and electrochemical surface area for the HER than NiS<sub>2</sub>/MoO<sub>2</sub>, W-NiS<sub>2</sub>, and W-MoO<sub>2</sub>. It is W doped NiS<sub>2</sub>/MoO<sub>2</sub>. It exhibits the heterojunctions between the NiS<sub>2</sub> and MoO<sub>2</sub> phases. It contains W, Ni, Mo, S, and O, which are homogeneously distributed. In the high-resolution XPS spectra, the Ni 2p peak of W-NiS<sub>2</sub>/MoO<sub>2</sub> exhibits a slight positive shift compared to that of NiS<sub>2</sub>. The Mo 3d peak of W-NiS<sub>2</sub>/MoO<sub>2</sub> exhibits a slight negative shift when compared to that of MoO<sub>2</sub>, suggesting a modified electronic structure in W-NiS<sub>2</sub>/MoO<sub>2</sub> possibly due to the partial transfer of electrons from NiS<sub>2</sub> to MoO<sub>2</sub>, which could be due to the higher electronegativity of Mo when compared to that of Ni. It contains mesopores. For the HER in 1 M KOH, it affords an  $\eta$  of -52 mV at -10 mA cm<sup>-2</sup>, suggesting its very high activity.

Fabrication of nickel sulfide/molybdenum sulfide as Mott-Schottky heterojunctions could lead to the spontaneous flow of electrons at the metal-semiconductor heterointerfaces till the work functions reach equilibrium on both sides, and that could modify the electronic structure, afford optimal adsorption energy with intermediates, improve the conductivity, which could boost the performance for the HER and OER. Gu *et al.*<sup>64</sup> observed that NiS/MoS<sub>2</sub> exhibits enhanced activity and stability for the HER and OER. It was obtained on pre-cleaned carbon cloth by a one-step hydrothermal treatment. NiS/MoS<sub>2</sub> exhibits higher activity, higher electrochemical surface area, and lower charge transfer resistance for the HER than NiS and MoS<sub>2</sub>. It is crystalline, containing hexagonal NiS and hexagonal MoS<sub>2</sub>, while it exhibits a heterojunction interface between NiS and

MoS<sub>2</sub>. It contains Mo, Ni, and S, which are homogeneously distributed. In the high-resolution XPS spectra, the Ni 2p peak of NiS/MoS<sub>2</sub> exhibits a slight negative shift compared to that of NiS. In contrast, Mo 3d peak of NiS/MoS<sub>2</sub> exhibits a slight positive shift compared to that of MoS<sub>2</sub>, suggesting a modified electronic structure possibly due to the partial transfer of electrons from MoS<sub>2</sub> to NiS. It exhibits superior hydrophilicity, having a water contact angle of 15.72°. It possesses a flower-like morphology due to a combination of numerous nanosheets. For the HER in 1 M KOH, it affords an  $\eta$  of -87 mV at -10 mA cm<sup>-2</sup>, suggesting its very high activity. For water splitting in 1 M KOH, NiS/MoS<sub>2</sub>//NiS/MoS<sub>2</sub> affords a potential of 1.51 V at 10 mA cm<sup>-2</sup>, suggesting its very high activity. At the same time, it exhibits 99.2% retention for 50 h, suggesting its very high stability. Besides, Yang *et al.*<sup>65</sup> observed that Ni<sub>3</sub>S<sub>2</sub>-MoS<sub>2</sub> exhibits enhanced activity and stability for the HER and OER. It was synthesized on pretreated Ni foam by a one-step hydrothermal treatment. Ni<sub>3</sub>S<sub>2</sub>-MoS<sub>2</sub> exhibits higher activity and lower charge transfer resistance for the HER than Ni<sub>3</sub>S<sub>2</sub> and MoS<sub>2</sub>. It is crystalline, containing Ni<sub>3</sub>S<sub>2</sub> and MoS<sub>2</sub> phases. It exhibits heterointerfaces between Ni<sub>3</sub>S<sub>2</sub> and MoS<sub>2</sub>. It contains Mo, Ni, and S, which are homogeneously distributed. In the high-resolution XPS spectra, the Ni 2p peak of Ni<sub>3</sub>S<sub>2</sub>-MoS<sub>2</sub> and Mo 3d peak of Ni<sub>3</sub>S<sub>2</sub>-MoS<sub>2</sub> showed a slight shift as compared to Ni<sub>3</sub>S<sub>2</sub> and MoS<sub>2</sub>, respectively, illustrating the modified electronic structure possibly due to the partial transfer of electrons between Ni<sub>3</sub>S<sub>2</sub> and MoS<sub>2</sub>. It exhibits 3D porous flower morphology, where the flower is composed of nanosheets.

Metal (oxy)hydroxides for the OER and metallic species for the HER are formed as the active species due to the dynamic structural reconstruction of heterostructured metallic sulfide/bimetallic sulfide pre-catalysts during water electrolysis to boost the performance for the HER and OER. Wu *et al.*<sup>66</sup> observed that Ni<sub>3</sub>S<sub>2</sub>/FeNi<sub>2</sub>S<sub>4</sub> showed high activity and stability for the HER and OER. It was synthesized on NiFe foam by the following steps: first, dual-scale porous NiFe foam was prepared by a redox process. After that, NiFeAl LDH was obtained on the pretreated NiFe foam by hydrothermal treatment. Finally, NiFeAl LDH was converted into Ni<sub>3</sub>S<sub>2</sub>/FeNi<sub>2</sub>S<sub>4</sub> by hydrothermal treatment. Ni<sub>3</sub>S<sub>2</sub>/FeNi<sub>2</sub>S<sub>4</sub> exhibits higher activity and lower charge transfer resistance for the HER and OER than NiFeAl LDH. It is crystalline, containing Ni<sub>3</sub>S<sub>2</sub> and FeNi<sub>2</sub>S<sub>4</sub> phases. It exhibits heterointerfaces between Ni<sub>3</sub>S<sub>2</sub> and FeNi<sub>2</sub>S<sub>4</sub>. It contains Fe, Ni, and S, which are homogeneously distributed, while it exhibits a trace amount of Al (3.4%). Ni<sub>3</sub>S<sub>2</sub>/FeNi<sub>2</sub>S<sub>4</sub> act as pre-catalysts, exhibiting dynamic structural reconstruction during water electrolysis, where the metallic Ni<sup>0</sup> for the HER and  $\gamma$ -NiOOH for the OER are the active species formed during electrolysis. It possesses porous, nanosheet array morphology. For the OER and HER in 1 M KOH, it affords an  $\eta$  of 201 mV at 10 mA cm<sup>-2</sup> and an  $\eta$  of -50 mV at -10 mA cm<sup>-2</sup>, respectively, showing its better activity. For overall water splitting in 1 M KOH, Ni<sub>3</sub>S<sub>2</sub>/FeNi<sub>2</sub>S<sub>4</sub>//Ni<sub>3</sub>S<sub>2</sub>/FeNi<sub>2</sub>S<sub>4</sub> affords a potential of 1.55 V at 10 mA cm<sup>-2</sup>, suggesting its very high activity.



Besides, Zhang *et al.*<sup>22</sup> observed that CuS-Ni<sub>3</sub>S<sub>2</sub>/CuNi exhibits enhanced activity and stability for the OER. It was obtained on pretreated Ni foam by electrodeposition followed by hydrothermal sulfurization. CuS-Ni<sub>3</sub>S<sub>2</sub>/CuNi exhibits higher activity, higher electrochemical surface area, and lower charge transfer resistance for the OER than Ni<sub>3</sub>S<sub>2</sub>/Ni. It is crystalline, containing CuS and Ni<sub>3</sub>S<sub>2</sub> phases, where CuS-Ni<sub>3</sub>S<sub>2</sub> is *in situ* grown on a CuNi alloy. It exhibits heterointerfaces between CuS and Ni<sub>3</sub>S<sub>2</sub>. It contains Ni, Cu, and S, which are homogeneously distributed. It contains macropores. For the OER in 1 M KOH, it affords an  $\eta$  of 337 mV at 100 mA cm<sup>-2</sup> and an  $\eta$  of 510 mV at a current density of 1000 mA cm<sup>-2</sup>, suggesting its very high activity, while it undergoes negligible decay at a current density of 1000 mA cm<sup>-2</sup> after 5000 cycles of CV, suggesting its high durability.

Moreover, Luo *et al.*<sup>67</sup> observed that MoS<sub>2</sub>-MoO<sub>3-x</sub>/Ni<sub>3</sub>S<sub>2</sub> exhibits enhanced activity and stability for the HER. It was prepared on Ni foam by a spontaneous chemical reaction at 80 °C followed by electrodeposition. MoS<sub>2</sub>-MoO<sub>3-x</sub>/Ni<sub>3</sub>S<sub>2</sub> exhibits higher activity and lower charge transfer resistance for the HER than MoS<sub>2</sub>, MoO<sub>3-x</sub>, and Ni<sub>3</sub>S<sub>2</sub>. It comprises a Ni<sub>3</sub>S<sub>2</sub> layer on Ni foam, which is covered by the MoS<sub>2</sub>-MoO<sub>3-x</sub> layer on the top. It exhibits a heterostructure. It has low crystallinity. It contains MoS<sub>2</sub> with abundant bridging S<sub>2</sub><sup>2-</sup> sites, MoO<sub>3-x</sub>, and Ni<sub>3</sub>S<sub>2</sub>, which could afford optimal adsorption energy with intermediates. For the HER in 1 M KOH, it affords an  $\eta$  of -76 mV at -10 mA cm<sup>-2</sup>, suggesting its very high activity.

In addition, Wang *et al.*<sup>68</sup> observed that Ni<sub>x</sub>S<sub>y</sub>@MnO<sub>x</sub>H<sub>y</sub> exhibits enhanced activity and stability for the HER and OER. It was obtained on pretreated Ni foam by hydrothermal sulfurization followed by anodic galvanostatic electrodeposition. Ni<sub>x</sub>S<sub>y</sub>@MnO<sub>x</sub>H<sub>y</sub> exhibits higher activity, higher electrochemical surface area, and lower charge transfer resistance for the HER and OER than Ni<sub>x</sub>S<sub>y</sub> and MnO<sub>x</sub>H<sub>y</sub>. It comprises a rod-like Ni<sub>x</sub>S<sub>y</sub>, surrounded by MnO<sub>x</sub>H<sub>y</sub>, where Ni<sub>x</sub>S<sub>y</sub> comprises Ni<sub>3</sub>S<sub>2</sub> and NiS phases. It exhibits a heterointerface between Ni<sub>x</sub>S<sub>y</sub> and MnO<sub>x</sub>H<sub>y</sub>. In the high-resolution XPS spectra, the Ni 2p peak of Ni<sub>x</sub>S<sub>y</sub>@MnO<sub>x</sub>H<sub>y</sub> exhibits a slight positive shift compared to that of Ni<sub>x</sub>S<sub>y</sub>, suggesting a modified electronic structure. Moreover, it contains Mn-O, Mn-Mn, and Mn-S bonds, where the existence of the Mn-S bond suggests the presence of electronic interaction at the heterointerface. It possesses a nanostructure. For the OER in 1 M KOH, it affords reasonable stability at 100 mA cm<sup>-2</sup> for 150 h, suggesting its very high stability, and it undergoes negligible decay at 500 mA cm<sup>-2</sup> after 5000 cycles of CV, suggesting its high durability. For the HER in 1 M KOH, it affords an  $\eta$  of -179 mV at -10 mA cm<sup>-2</sup>, suggesting its very high activity, while it affords reasonable stability at -100 mA cm<sup>-2</sup> for 100 h, suggesting its very high stability. For overall water splitting in 1 M KOH, Ni<sub>x</sub>S<sub>y</sub>@MnO<sub>x</sub>H<sub>y</sub>/Ni<sub>x</sub>S<sub>y</sub>@MnO<sub>x</sub>H<sub>y</sub> affords a potential of 1.53 V at 10 mA cm<sup>-2</sup>, suggesting its very high activity. In contrast, it undergoes negligible decay at 100 mA cm<sup>-2</sup> for 100 h, suggesting its very high stability.

Moreover, Che *et al.*<sup>69</sup> observed that (Ni-Fe)<sub>x</sub>/NiFe(OH)<sub>y</sub> exhibits enhanced activity and stability for the HER and OER. It was obtained on pretreated Ni foam by the one-step electrodeposition method at room temperature. (Ni-Fe)<sub>x</sub>/NiFe(OH)<sub>y</sub> exhibits higher activity for the HER and OER than Fe<sub>0.96</sub>S/Fe(OH)<sub>3</sub>. It is an amorphous (Ni-Fe)<sub>x</sub>/NiFe(OH)<sub>y</sub> composite. It possesses micro/nano-architecture, and exhibits high wettability with a water contact angle of  $\leq 0^\circ$ , suggesting its super-aerophobic properties, which could facilitate the evolution of gas. For the OER in 1 M KOH, it affords an  $\eta$  of 199 mV at 10 mA cm<sup>-2</sup> and an  $\eta$  of  $\sim 510$  mV at a current density of 1000 mA cm<sup>-2</sup>, suggesting its very high activity. For overall water splitting in 1 M KOH, (Ni-Fe)<sub>x</sub>/NiFe(OH)<sub>y</sub>/(Ni-Fe)<sub>x</sub>/NiFe(OH)<sub>y</sub> affords a potential of 1.46 V at 10 mA cm<sup>-2</sup>, suggesting its very high activity.

In addition, Lu *et al.*<sup>70</sup> observed that FeCoS<sub>x</sub>-PBA exhibits enhanced activity and stability for the OER, where FeCoS<sub>x</sub>-PBA is composed of amorphous FeCoS<sub>x</sub>, which is embedded in Prussian blue analog hetero-nanoframes. It possesses a hollow cubic-like morphology, where plenty of nanoparticles are attached to the cubic surface. It contains two forms of S atom, where one is S<sup>2-</sup> in FeCoS<sub>x</sub>, while the other is S-doped PBA. In the high-resolution XPS spectra, the Fe 2p peak of FeCoS<sub>x</sub>-PBA exhibits a slight shift when compared to that of mixed PBA, suggesting a modified electronic structure in FeCoS<sub>x</sub>-PBA. The following steps are involved in the synthesis: first, PBA was obtained by the precipitation method. Then, mixed PBA was prepared by an ultrasound-assisted ion exchange route. Finally, FeCoS<sub>x</sub>-PBA was obtained by solvothermal treatment. FeCoS<sub>x</sub>-PBA exhibits higher activity, higher electrochemical surface area, and lower charge transfer resistance for the OER PBA and mixed PBA.

The incorporation of Ni in iron thiophosphate could tune the electronic structure and increase the electronic conductivity, and that could enhance the activity for the HER and OER. Tang *et al.*<sup>71</sup> observed that Ni-FePS<sub>3</sub> exhibits enhanced activity and stability for the HER and OER in 1 M KOH. It was prepared by impregnation-adsorption followed by annealing at 450 °C for 5 minutes in an Ar atmosphere. The Ni-FePS<sub>3</sub> exhibits higher activity for the HER and OER than Co-FePS<sub>3</sub>, Pd-FePS<sub>3</sub>, and FePS<sub>3</sub>. The differential electron density of Ni-FePS<sub>3</sub> (Structure 1 as shown in Fig. 2a and Structure 2 as shown in Fig. 2b) are provided to understand the causes of the interaction of Ni atom with FePS<sub>3</sub>, which enhances the catalysis. The interaction of the Ni atom with FePS<sub>3</sub> in Ni-FePS<sub>3</sub> leads to the flow of electrons of the Fe atom, preferably towards the opposite Ni-S bonding, which causes a large negative charge on S and lesser electron density on Fe, as shown in Fig. 2a. In the same way, the charge distribution at the Ni-S bond changes when the charge of the S atom increases to -0.45 from -0.38, as shown in Fig. 2b. Moreover, the charge of Fe atoms near the Ni atom linked by edge S atom sharing (Fe-S-Ni) increases to 0.74 from 0.7. Structure 2 is considered a more suitable configuration because it exhibits lower formation energy than Structure 1. The



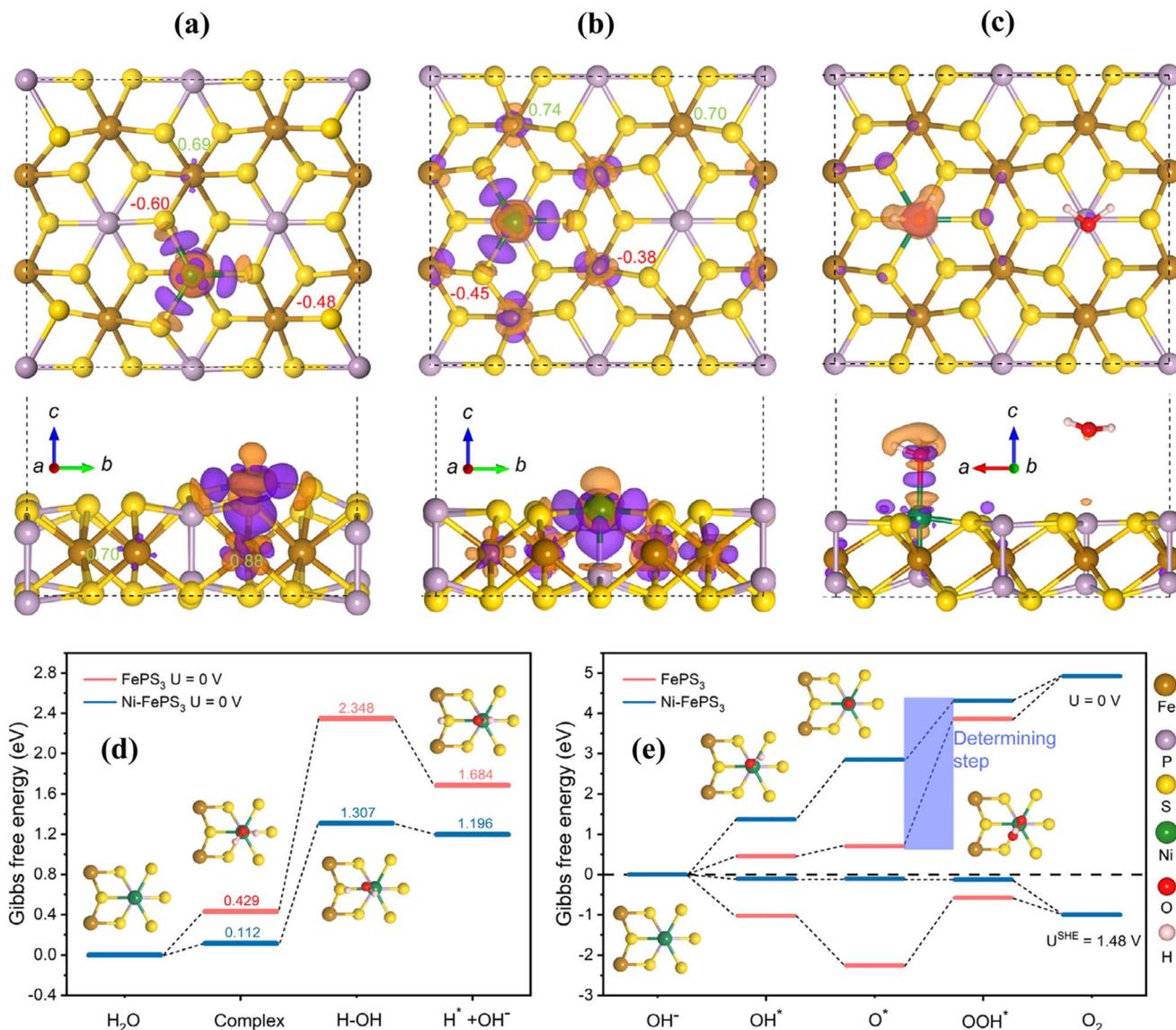


Fig. 2 Differential electron density (top-view and side-view) of (a) Structure 1 and (b) Structure 2 of Ni-FePS<sub>3</sub> (iso-surface value: 0.005 eBohr<sup>-3</sup>), where the red and green color numbers indicate Bader charge numbers of S and Fe, respectively; (c) differential electron density (top-view and side-view) of water adsorbed on the basal plane of Ni-FePS<sub>3</sub> (iso-surface value: 0.002 eBohr<sup>-3</sup>); Gibbs free energy profiles of Ni-FePS<sub>3</sub> in comparison with FePS<sub>3</sub> for the (d) HER and (e) OER (reproduced with permission from ref. 71 Copyright 2021, Zhengzhou University).

outbound H<sub>2</sub>O adsorption behavior on Ni sites of Ni-FePS<sub>3</sub> for the HER was disclosed by the differential electron density (Fig. 2c). Fig. 2d depicts the calculated Gibbs free energy profiles and the proposed reaction mechanism for the HER. Ni-FePS<sub>3</sub> exhibits lower water adsorption energy (0.11 eV) and lesser water dissociation energy barrier (1.2 eV), suggesting its enhanced HER catalysis. In contrast, FePS<sub>3</sub> exhibits higher water adsorption energy (0.43 eV) and a more enormous water dissociation energy barrier (1.92 eV), suggesting its sluggish HER catalysis. The water adsorption/dissociation configurations on Ni-FePS<sub>3</sub> suggest that water molecules could be

adsorbed on the Ni sites, where the water dissociation could be supported by the nearby S sites having increased electron density. Fig. 2e depicts the calculated Gibbs free energy profiles and the proposed reaction mechanism for the OER. The Ni atoms with charge enrichment in Ni-FePS<sub>3</sub> could serve as active sites to more suitably weaken the rate-limiting O<sup>•</sup> intermediates compared to the P sites in the FePS<sub>3</sub>. Ni-FePS<sub>3</sub> comprises the monoclinic phase of FePS<sub>3</sub>, anchored by atomically dispersed Ni atoms. The characteristic peak corresponding to Ni-Ni bonding at about 2.48 Å was not observed for Ni-FePS<sub>3</sub> from the Ni K-edge EXAFS spectra, suggesting the existence of Ni



predominantly as a single atomic species in Ni-FePS<sub>3</sub>. The Fe K-edge XANES spectra disclose that the near-edge absorption energy of Ni-FePS<sub>3</sub> is higher than that of FePS<sub>3</sub> and Fe foil, suggesting that the average electron density around Fe in Ni-FePS<sub>3</sub> is less than that of FePS<sub>3</sub> and Fe foil. In the high-resolution XPS spectra of S 2p, Ni-FePS<sub>3</sub> exhibits a slight negative shift (0.2 eV) when compared to FePS<sub>3</sub>, suggesting the modified electronic structure after Ni incorporation in FePS<sub>3</sub>. The projected density of states discloses the formation of some new electronic states for Ni-FePS<sub>3</sub> due to the hybridization of Fe 3d, S 2p, and Ni 3d in the bandgap, which could be due to the charge redistribution, suggesting the higher electronic conductivity after Ni incorporation in FePS<sub>3</sub>. Ni, Fe, P, and S possess nanosheet morphology and are distributed homogeneously. Thus, incorporation of Ni in FePS<sub>3</sub> could modify the electronic structure and improve the electronic conductivity, and that could enhance the activity for the HER and OER.

Besides, Yang *et al.*<sup>72</sup> observed that Ni<sub>2</sub>P-Ni<sub>12</sub>P<sub>5</sub>@Ni<sub>3</sub>S<sub>2</sub> exhibits enhanced activity and stability for the HER. It was obtained on cleaned Ni foam by hydrothermal treatment for simultaneous corrosion and sulfidation followed by phosphidation at 370 °C for 2 h under an N<sub>2</sub> atmosphere. Ni<sub>2</sub>P-Ni<sub>12</sub>-P<sub>5</sub>@Ni<sub>3</sub>S<sub>2</sub> exhibits higher activity, higher electrochemical surface area, and lower charge transfer resistance for the HER than Ni<sub>2</sub>P. It comprises a Ni<sub>2</sub>P-Ni<sub>12</sub>P<sub>5</sub> nanorod array, which is rooted in Ni<sub>3</sub>S<sub>2</sub> film. It exhibits a heterointerface between Ni<sub>2</sub>P and Ni<sub>12</sub>P<sub>5</sub> phases. It exhibits super hydrophilicity with a contact angle of 0°. For the HER in 1 M KOH, it affords an  $\eta$  of -32 mV at -10 mA cm<sup>-2</sup>, suggesting its very high activity.

Moreover, Paudel *et al.*<sup>73</sup> observed that the 1T Co-WS<sub>2</sub>/NiTe<sub>2</sub>/Ni exhibits enhanced activity and stability for the HER and OER. It was obtained on pretreated Ni foam by a two-step hydrothermal treatment. The 1T Co-WS<sub>2</sub>/NiTe<sub>2</sub>/Ni exhibits higher activity and lower charge transfer resistance for the HER than WS<sub>2</sub>/NiTe<sub>2</sub>/Ni, WS<sub>2</sub>/Ni, and 1T NiTe<sub>2</sub>/Ni. 1T Co-WS<sub>2</sub>/NiTe<sub>2</sub>/Ni exhibits higher activity and electrochemical surface area for the OER than WS<sub>2</sub>/NiTe<sub>2</sub>/Ni, WS<sub>2</sub>/Ni, and 1T NiTe<sub>2</sub>/Ni. It comprises a metallic NiTe<sub>2</sub>/Ni nanoskeleton as the core and a Co-WS<sub>2</sub> nanosheet layer as the shell. It exhibits a heterointerface between the WS<sub>2</sub> and NiTe<sub>2</sub> phases. For the HER in 1 M KOH, it affords an  $\eta$  of -88 mV at -10 mA cm<sup>-2</sup>, suggesting its very high activity. For overall water splitting in 1 M KOH, the 1T Co-WS<sub>2</sub>/NiTe<sub>2</sub>/Ni//1T Co-WS<sub>2</sub>/NiTe<sub>2</sub>/Ni affords a potential of 1.521 V at 10 mA cm<sup>-2</sup>, suggesting its high activity.

Fabrication of electrocatalysts with high valence state sites could act as favorable reductive centers for large-current-density water splitting. Li *et al.*<sup>74</sup> proposed that a high valence state of Co<sup>3+</sup> in the Ni<sub>9.5</sub>Co<sub>0.5</sub>-S-FeO<sub>x</sub> hybrid catalyst can act as a favorable center for a stable and efficient HER compared to the hybrid catalyst with low chemical states. At the same time, it was obtained on Cu foam through a two-step electrodeposition method. For the HER in 1 M KOH at 60 °C, it affords an  $\eta$  of -22 mV at -10 mA cm<sup>-2</sup> and an  $\eta$  of -175 mV at a current density of -1000 mA cm<sup>-2</sup>, suggesting its very high activity. For overall water splitting in 1 M KOH at 60 °C, Ni<sub>9.5</sub>Co<sub>0.5</sub>-S-FeO<sub>x</sub>//

Ni<sub>9.5</sub>Co<sub>0.5</sub>-S-FeO<sub>x</sub> affords a potential of 1.730 V at a current density of 1000 mA cm<sup>-2</sup>, suggesting its very high activity, while it exhibits high stability.

Coupling of the suitable transition metal atoms with the nanostructured Chevrel-phase metal sulfides could cause the delocalization of d-electrons, enhance the charge transfer, afford optimal adsorption energies with intermediates, and that could enhance the performance for the HER and OER. Chandrasekaran *et al.*<sup>75</sup> demonstrated that Co/N-NiMo<sub>3</sub>S<sub>4</sub> exhibits high activity and stability for the HER and OER while it was prepared by hydrothermal treatment. Theoretical and experimental investigation discloses that delocalization of the d-electron on Co/N-NiMo<sub>3</sub>S<sub>4</sub> can occur due to the coupling of Co atoms with edge Ni atoms, leading to enhancement in charge transfer, which could enhance the performance for overall water electrolysis. Moreover, an upshift in the d-band center of Co/N-NiMo<sub>3</sub>S<sub>4</sub> can provide optimal adsorption energies for the intermediates for water dissociation and adsorption, enhancing overall water electrolysis. For the HER in 1 M KOH, it affords an  $\eta$  of -78 mV at -10 mA cm<sup>-2</sup> and an  $\eta$  of -307 mV at a high current density of -1000 mA cm<sup>-2</sup>, suggesting its very high activity. For the OER in 1 M KOH, it affords an  $\eta$  of 186 mV at 50 mA cm<sup>-2</sup> and an  $\eta$  of 225 mV at 300 mA cm<sup>-2</sup>, suggesting its very high activity. For overall water splitting in 1 M KOH, Co/N-NiMo<sub>3</sub>S<sub>4</sub>//Co/N-NiMo<sub>3</sub>S<sub>4</sub> affords a potential of 1.47 V at 10 mA cm<sup>-2</sup>, suggesting its very high activity while it exhibits high stability.

**2.2.2. Fabricating selenide electrocatalysts.** Fabrication of heterostructured transition metal selenide/metal selenide having a nanostructure could modify the electronic structure, provide optimal adsorption energy with intermediates, facilitate the evolution of gas, and that could enhance the performance of the HER and OER. Majumdar *et al.*<sup>76</sup> observed that MoSe<sub>2</sub>@NiCo<sub>2</sub>Se<sub>4</sub> exhibits enhanced activity for the HER and OER. It was obtained on pretreated Ni foam by hydrothermal treatment followed by hydrothermal selenization at 140 °C for 2 h. MoSe<sub>2</sub>@NiCo<sub>2</sub>Se<sub>4</sub> exhibits higher activity and lower charge transfer resistance for the HER and OER than MoO<sub>3</sub>/NiCo(OH)<sub>2</sub>. It is a MoSe<sub>2</sub>@NiCo<sub>2</sub>Se<sub>4</sub> heterostructure. It possesses a nanosheet on nanosheet structure. For the HER in 1 M KOH, it affords an  $\eta$  of -89 mV at -10 mA cm<sup>-2</sup>, suggesting its very high activity.

Fabrication of transition bimetallic doped selenides could modify the electronic structure and provide optimal adsorption energy with intermediates, enhancing the performance for the HER and OER. Ibraheem *et al.*<sup>77</sup> observed that Fe@Co/Se<sub>2</sub> exhibits enhanced activity and stability for the HER and OER. It was obtained by hydrothermal treatment. Fe@Co/Se<sub>2</sub> exhibits higher activity and lower charge transfer resistance for the HER and OER than Fe-Se<sub>2</sub> and Co-Se<sub>2</sub>. It is crystalline, containing an Fe, Co dual doped selenide. It contains Co, Fe, and Se, which are homogeneously distributed. In the high-resolution XPS spectra, the Fe 2p peak of Fe@Co/Se<sub>2</sub> exhibits a slight positive shift when compared to that of Fe-Se<sub>2</sub>. In contrast, the Co 2p peak of Fe@Co/Se<sub>2</sub> exhibits a slight negative shift when compared to



that of Co-Se<sub>2</sub>, suggesting a modified electronic structure, possibly due to the partial transfer of electrons from the Fe to Co, which could be due to the higher electronegativity of Co, when compared to that of Fe. It contains Fe<sup>2+/3+</sup>/Co<sup>2+</sup> species, which are coupled to selenide utilizing an Fe-coordinated Co-bridged bond. It possesses nanorod morphology. For the OER in 1 M KOH, it affords an  $\eta$  of 200 mV at 10 mA cm<sup>-2</sup>, suggesting its very high activity. For the HER in 1 M KOH, it affords an  $\eta$  of -78 mV at -10 mA cm<sup>-2</sup>, suggesting its very high activity. For overall water splitting in 1 M KOH, Fe@Co/Se<sub>2</sub>/Fe@Co/Se<sub>2</sub> affords a potential of 1.51 V at 10 mA cm<sup>-2</sup>, suggesting its very high activity.

Fabrication of nanostructured tungsten incorporated CoSe/Co<sub>3</sub>O<sub>4</sub> could modify the electronic structure, afford optimal adsorption energy with intermediates, facilitate the gas evolution, and expose abundant active sites, and that could enhance the activity and stability for the HER and OER. Balaji *et al.*<sup>78</sup> observed that WCoSe/WCo<sub>3</sub>O<sub>4</sub> exhibits very high activity and stability for the HER and OER. It was synthesized on Ni foam by hydrothermal treatment at ~160 °C for 16 h followed by selenization at ~180 °C for 4 h followed by calcination at 300 °C for

2 h in an air atmosphere. WCoSe/WCo<sub>3</sub>O<sub>4</sub> exhibits higher activity and electrochemical surface area for the HER and OER than WSe<sub>2</sub>/WO<sub>2</sub> and CoSe/Co<sub>3</sub>O<sub>4</sub>. It possesses a nanosheet-like structure having nanopores (Fig. 3a). It is polycrystalline (Fig. 3b). It contains WSe<sub>2</sub>, WO<sub>2</sub>, CoSe, and Co<sub>3</sub>O<sub>4</sub> phases, while it exhibits heterointerfaces (Fig. 3c). It exhibits a high crystalline structure (Fig. 3d). It contains W, Co, Se, and O (Fig. 3e). In the XPS spectra, the W 4f peak for WCoSe/WCo<sub>3</sub>O<sub>4</sub> is slightly shifted towards higher binding energy when compared to that of WSe<sub>2</sub>/WO<sub>2</sub>, suggesting a modified electronic structure. For the OER in 1 M KOH, it affords an  $\eta$  of 175 mV at 10 mA cm<sup>-2</sup>, suggesting its very high activity. For the HER in 1 M KOH, it affords an  $\eta$  of -98 mV at -10 mA cm<sup>-2</sup>, suggesting its very high activity. For overall water splitting in 1 M KOH, WCoSe/WCo<sub>3</sub>O<sub>4</sub>/WCoSe/WCo<sub>3</sub>O<sub>4</sub> affords a potential of 1.49 V at 10 mA cm<sup>-2</sup>, suggesting its very high activity. In contrast, it affords reasonable stability at 100 mA cm<sup>-2</sup> for 100 h, suggesting its high stability.

Selenization of stainless steel followed by heat treatment followed by electrochemical oxidation could create abundant oxygen vacancies, increase the Ni content, and that could enhance the performance of the OER. Han *et al.*<sup>79</sup> observed that

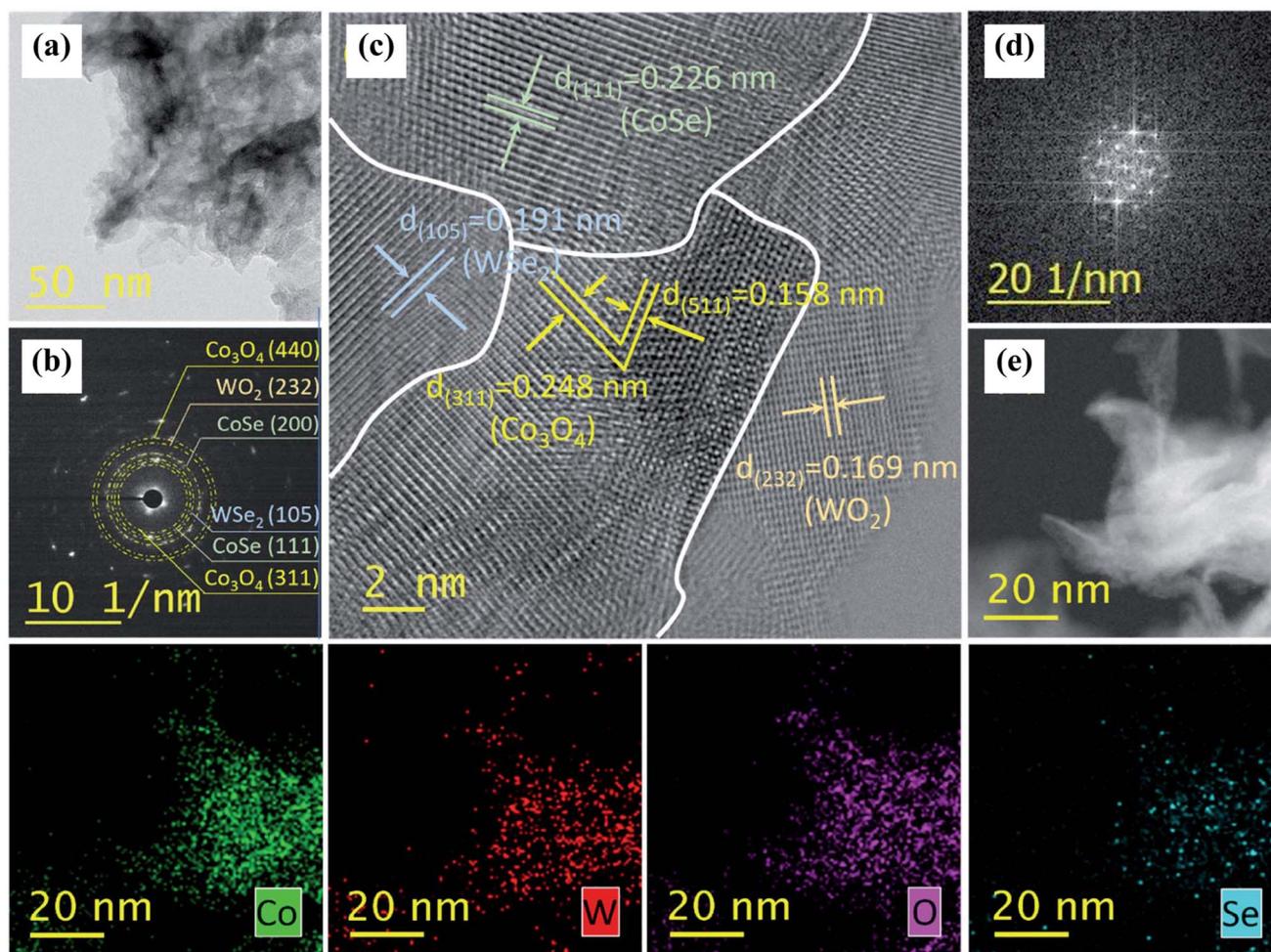


Fig. 3 Characterization of the WCoSe/WCo<sub>3</sub>O<sub>4</sub> heterostructure: (a) TEM image; (b) SAED pattern; (c) HRTEM image; (d) FFT pattern; (e) STEM image and its corresponding EDS elemental mapping (reproduced with permission from ref. 78 Copyright 2022, The Royal Society of Chemistry).



SS-500-AO exhibits enhanced activity and stability for the OER. SS-500-AO is an electrocatalyst on SUS304 stainless steel, where the catalyst was prepared by selenization followed by heat treatment followed by electrochemical oxidation. It contains abundant oxygen vacancies (76.09%). It contains 51.18% of Ni<sup>3+</sup>, 12.72% of Ni<sup>2+</sup>, and 36.1% of metallic Ni. For the OER in 1 M KOH, it affords an  $\eta$  of 284.3 mV at 10 mA cm<sup>-2</sup>, suggesting its very high activity, while it undergoes negligible decay at 10 mA cm<sup>-2</sup> for 160 h, suggesting its very high stability.

Fabrication of composites containing transition metal selenides and perovskite oxides could enhance the performance of the HER and OER. Kim *et al.*<sup>9</sup> observed that LSCO-MoSe<sub>2</sub> exhibits enhanced activity for the HER and OER, where LSCO is La<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3- $\delta$</sub>  perovskite oxide. It was prepared by a sol-gel process followed by calcination followed by ball milling. Fabrication of composites containing transition metal selenides, N-doped graphene quantum dots, and perovskite oxides could modify the electronic structure, afford optimal adsorption energy with intermediates, enhance the conductivity, and that could enhance the performance for the HER and OER. Cao *et al.*<sup>80</sup> observed that LSC-N-GQDs-MoSe<sub>2</sub> exhibits enhanced activity and stability for the HER and OER (LSC: La<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3- $\delta$</sub> ; N-GQDs: N-doped graphene quantum dots). It is a composite containing a thin layer of N-GQDs (thickness: 2 to 3 nm) at the interface of LSC and MoSe<sub>2</sub>. In the high-resolution XPS spectra, the La 3d and Co 2p peaks of LSC-N-GQDs-MoSe<sub>2</sub> exhibit a slight positive shift when compared to that of LSC, suggesting a modified electronic structure. LSC-N-GQDs-MoSe<sub>2</sub> exhibits higher activity and lower charge transfer resistance for the HER and OER than LSC-MoSe<sub>2</sub>. For overall water splitting in 1 M KOH, LSC-N-GQDs-MoSe<sub>2</sub>//LSC-N-GQDs-MoSe<sub>2</sub> affords a potential of ~1.57 V at 10 mA cm<sup>-2</sup>, suggesting its very high activity, while it undergoes negligible decay at 500 mA cm<sup>-2</sup> for 24 h, suggesting its very high stability. The following steps were used in its preparation: at first, N-GQDs were obtained by hydrothermal treatment, and the LSC was synthesized by a sol-gel process followed by calcination. Then, LSC-N-GQDs were obtained by sonication of the LSC and N-GQDs. Later, MoSe<sub>2</sub> was obtained by ball milling. Finally, LSC-N-GQDs-MoSe<sub>2</sub> was prepared by ball milling the LSC-N-GQDs and MoSe<sub>2</sub>.

Ion irradiation could activate the inert basal plane of MoSe<sub>2</sub>, and that could enhance the performance of the HER. Huang *et al.*<sup>81</sup> demonstrated that the activity of MoSe<sub>2</sub> nanosheet arrays was activated by He<sup>+</sup> ion irradiation, which could generate multiple vacancies in the inert basal planes. DFT studies disclose that the increase in electrical conductivity and reduction in energy barriers for water dissociation and subsequent proton adsorption can be due to the existence of single Mo and single Se vacancies on the basal plane of MoSe<sub>2</sub>, which could enhance HER performance. For the HER in 1 M KOH, it affords an  $\eta$  of -90 mV at -10 mA cm<sup>-2</sup>, suggesting its very high activity, while it exhibits high stability at a current density of 1000 mA cm<sup>-2</sup>.

### 2.3. Fabricating metal phosphide/phosphate electrocatalysts

Fabrication of nickel phosphide nanoarrays with a super-aerophobic surface could facilitate the gas evolution, expose abundant active sites, enhance the conductivity, and that could enhance the performance for the HER. Yu *et al.*<sup>82</sup> observed that Ni<sub>2</sub>P exhibits enhanced activity and stability for the HER. It was prepared by two-step hydrothermal treatment followed by phosphorization at 300 °C for 30 min under Ar atmosphere. The Ni<sub>2</sub>P exhibits higher activity, higher electrochemical surface area, and lower charge transfer resistance for the HER than Ni(OH)<sub>2</sub>. It is hexagonal Ni<sub>2</sub>P. It contains Ni and P, which are homogeneously distributed. It possesses nanoarray morphology. It exhibits a superaerophobic surface, which could facilitate the evolution of gas. For the HER in 1 M KOH, it affords an  $\eta$  of -37 mV at -10 mA cm<sup>-2</sup> and an  $\eta$  of -306 mV at current density of -1000 mA cm<sup>-2</sup>, suggesting its very high activity, and it undergoes negligible decay at -1200 mA cm<sup>-2</sup> after 5000 cycles of CV, suggesting its high durability. For overall water splitting in 1 M KOH, the NiFe LDH<sup>OER</sup>//Ni<sub>2</sub>P<sup>HER</sup> affords a potential of ~2.05 V at a current density of 1000 mA cm<sup>-2</sup>, suggesting its very high activity.

Fabrication of transition bimetallic phosphides could modify the electronic structure, afford optimal adsorption energy with intermediates, and enhance the performance of the HER and OER. Zhao *et al.*<sup>83</sup> observed that NiCoP exhibits enhanced activity and stability for the HER and OER. It was synthesized by ultrasonic agitation followed by phosphorization at 350 °C for 3 h. NiCoP exhibits higher activity, higher electrochemical surface area, and lower charge transfer resistance for the HER and OER than CoP. It is quasi-monolayered Ni5% CoP. It contains Ni, Co, and P, which are homogeneously distributed. In the high-resolution XPS spectra, the P 2p peaks of NiCoP exhibit a slight negative shift compared to that of CoP, suggesting a modified electronic structure. It possesses a 2D sub-nanostructure. It contains abundant mesopores. For the OER in 1 M KOH, it affords an  $\eta$  of 259 mV at 10 mA cm<sup>-2</sup>, suggesting its very high activity, and it undergoes negligible decay at 90 mA cm<sup>-2</sup> after 10 000 cycles of CV, suggesting its high durability. For the HER in 1 M KOH, it affords an  $\eta$  of -84 mV at -10 mA cm<sup>-2</sup>, suggesting its very high activity, and it undergoes slight decay at -140 mA cm<sup>-2</sup> after 10 000 cycles of CV, suggesting its high durability. For overall water splitting in 1 M KOH, the NiCoP//NiCoP affords a potential of 1.48 V at 10 mA cm<sup>-2</sup>, suggesting its very high activity. Moreover, Song *et al.*<sup>84</sup> observed that CoNiP exhibits enhanced activity for the HER and OER. It was prepared by ion exchange/etching of ZIF-67 (Co-based zeolitic imidazolate frameworks) followed by phosphidation. CoNiP exhibits higher activity for the HER and OER than that of CoNi LDH. It is crystalline, containing nanostructured CoNiP. It contains Ni, Co, P, and C, which are homogeneously distributed. In the high-resolution XPS spectra, the Ni 2p and Co 2p peaks of CoNiP exhibit a slight shift compared to that of CoNi LDH, suggesting a modified electronic structure.



Nanostructured Fe-doped CoP can be prepared by the phosphorization of a bimetallic Prussian blue analog, and that could facilitate the evolution of gas, enhance the conductivity, which could enhance the performance for the HER and OER. Cao *et al.*<sup>85</sup> observed that the Fe-CoP exhibits enhanced activity and stability for the HER and OER. It was obtained on pre-treated Ni foam by co-precipitation followed by phosphorization at 400 °C for 3 h under an N<sub>2</sub> atmosphere. Fe-CoP exhibits higher activity and lower charge transfer resistance for the HER and OER than CoFe<sub>2</sub>O<sub>4</sub>. It is Fe-doped CoP. It contains Fe, Co, P, O, and C, which are homogeneously distributed. It possesses a hierarchical nanoporous structure, where the crystalline nanoparticles are embedded in amorphous carbon layers. It possesses a high specific surface area of 177 m<sup>2</sup> g<sup>-1</sup>. It contains mesopores and macropores. For the OER in 1 M KOH, it affords an  $\eta$  of 190 mV at 10 mA cm<sup>-2</sup> and an  $\eta$  of 428 mV at a current density of 1000 mA cm<sup>-2</sup>, suggesting its very high activity, while it undergoes negligible decay at 1000 mA cm<sup>-2</sup> for 30 h, suggesting its very high stability. For the HER in 1 M KOH, it affords an  $\eta$  of -78 mV at -10 mA cm<sup>-2</sup>, suggesting its very high activity. For overall water splitting in 1 M KOH, Fe-CoP//Fe-CoP affords a potential of 1.49 V at 10 mA cm<sup>-2</sup>, suggesting its very high activity.

Fabrication of the nanostructured trimetallic MnNiCo phosphide could modify the electronic structure, provide optimal adsorption energy with intermediates, facilitate the evolution of gas, enhance the conductivity, expose abundant active sites, and that could enhance the performance for the HER and OER. Salem *et al.*<sup>10</sup> observed that Mn<sub>1</sub>Ni<sub>1</sub>Co<sub>1</sub>-P exhibits enhanced activity and stability for the HER and OER. It was obtained on Ni foam by electrodeposition followed by plasma phosphidation at 250 °C for 3 h under a PH<sub>3</sub>/Ar atmosphere. Mn<sub>1</sub>Ni<sub>1</sub>Co<sub>1</sub>-P exhibits higher activity, higher electrochemical surface area, and lower charge transfer resistance for the HER and OER than MnNiCo-OH. It is trimetallic Mn<sub>1</sub>Ni<sub>1</sub>Co<sub>1</sub>-P, containing hexagonal NiCoP. It contains Ni, Mn, Co, and P, which are homogeneously distributed. In the high-resolution XPS spectra, the P 2p peak of Mn<sub>1</sub>Ni<sub>1</sub>Co<sub>1</sub>-P exhibits a slight negative shift when compared to that of phosphorus, suggesting a modified electronic structure possibly due to the strong interaction between the metals and the P atom. It possesses an interconnected nanosheet structure. For the OER in 1 M KOH, it affords an  $\eta$  of 289 mV at 10 mA cm<sup>-2</sup>, suggesting its very high activity, and it undergoes negligible decay at 10 mA cm<sup>-2</sup> after 5000 cycles of CV, suggesting its high durability. For the HER in 1 M KOH, it affords an  $\eta$  of -14 mV at -10 mA cm<sup>-2</sup>, suggesting its substantially very high activity, and it undergoes negligible decay at -10 mA cm<sup>-2</sup> after 5000 cycles of CV, suggesting its high durability. For overall water splitting in 1 M KOH, Mn<sub>1</sub>-Ni<sub>1</sub>Co<sub>1</sub>-P//Mn<sub>1</sub>Ni<sub>1</sub>Co<sub>1</sub>-P affords a potential of 1.48 V at 10 mA cm<sup>-2</sup>, suggesting its very high activity.

Besides, Wu *et al.*<sup>19</sup> observed that Ni<sub>2</sub>P-Fe<sub>2</sub>P exhibits enhanced activity and stability for the HER and OER. The following steps were employed to obtain it. At first, Ni(OH)<sub>2</sub> was prepared on cleaned Ni foam by the etching growth method at

room temperature. Then, Ni(OH)<sub>2</sub> was converted into (Ni,Fe)(OH)<sub>2</sub> by an ion-exchange process at room temperature. Finally, (Ni,Fe)(OH)<sub>2</sub> was converted into Ni<sub>2</sub>P-Fe<sub>2</sub>P by phosphidation at 450 °C for 1.5 h under an Ar atmosphere. Ni<sub>2</sub>P-Fe<sub>2</sub>P exhibits higher activity, higher electrochemical surface area, and lower charge transfer resistance for the HER and OER than Ni(OH)<sub>2</sub> and Ni<sub>2</sub>P-Ni<sub>5</sub>P<sub>4</sub>. It is crystalline, containing Ni<sub>2</sub>P and Fe<sub>2</sub>P phases. It exhibits a heterostructure. It contains Fe, Ni, and P, which are homogeneously distributed. It possesses micro-sheet morphology having a thickness of about 7.4 nm. For the OER in 1 M KOH, it affords an  $\eta$  of 218 mV at 10 mA cm<sup>-2</sup> and an  $\eta$  of 337 mV at a current density of 1000 mA cm<sup>-2</sup>, suggesting its very high activity, and it undergoes negligible decay at 1000 mA cm<sup>-2</sup> after 3000 cycles of CV, suggesting its high durability. For the HER in 1 M KOH, it affords an  $\eta$  of -128 mV at -10 mA cm<sup>-2</sup> and an  $\eta$  of -333 mV at a current density of -1000 mA cm<sup>-2</sup>, suggesting its very high activity, and it undergoes negligible decay at -1000 mA cm<sup>-2</sup> after 3000 cycles of CV, suggesting its high durability. For overall water splitting in 1 M KOH, Ni<sub>2</sub>P-Fe<sub>2</sub>P//Ni<sub>2</sub>P-Fe<sub>2</sub>P affords a potential of 1.561 V at 10 mA cm<sup>-2</sup> and ~1.98 V at a current density of 1000 mA cm<sup>-2</sup>, suggesting its very high activity.

Moreover, Yu *et al.*<sup>18</sup> observed that FeP/Ni<sub>2</sub>P exhibits significantly very high activity and stability for the HER and OER. It was prepared on Ni foam by a two-step phosphidation process. FeP/Ni<sub>2</sub>P exhibits higher activity and electrochemical surface area for the HER than Ni<sub>2</sub>P\*, while it exhibits higher activity and electrochemical surface area for the OER than Ni<sub>2</sub>P. It exhibits lower charge transfer resistance than Ni<sub>2</sub>P for the HER and OER. FeP/Ni<sub>2</sub>P possesses mesopores and/or nanopores (Fig. 4a and b). It possesses nanoparticle morphology. It is crystalline and contains FeP and Ni<sub>2</sub>P phases (Fig. 4c, d and g). It contains Ni, Fe, and P, which are homogeneously distributed (Fig. 4e). It is a metal phosphide (Fig. 4f). Thus, the nanostructured transition hybrid metal phosphides with pores on 3D Ni foam could modify the electronic structure, provide optimal adsorption energy with intermediates, enhance the conductivity, facilitate the gas evolution, and expose abundant active sites, and that could enhance the activity and stability for the HER and OER. For the OER in 1 M KOH, it affords an  $\eta$  of 154 mV at 10 mA cm<sup>-2</sup> and an  $\eta$  of 293 mV at a current density of 1000 mA cm<sup>-2</sup>, suggesting its outstanding activity, while it undergoes negligible decay at a current density of 1500 mA cm<sup>-2</sup> after 5000 cycles of CV, suggesting its outstanding durability. For the HER in 1 M KOH, it affords an  $\eta$  of -14 mV at -10 mA cm<sup>-2</sup> and an  $\eta$  of ~-270 mV at a current density of -1000 mA cm<sup>-2</sup>, suggesting its outstanding activity, while it undergoes negligible decay at -1000 mA cm<sup>-2</sup> after 5000 cycles of CV, suggesting its outstanding durability. For overall water splitting in 1 M KOH, FeP/Ni<sub>2</sub>P//FeP/Ni<sub>2</sub>P affords a potential of 1.42 V at 10 mA cm<sup>-2</sup> and a potential of ~1.78 V at a current density of 1000 mA cm<sup>-2</sup> (Fig. 4h), suggesting its outstanding activity, while it undergoes negligible decay at 500 mA cm<sup>-2</sup> for >40 h (Fig. 4i), suggesting its very high stability.



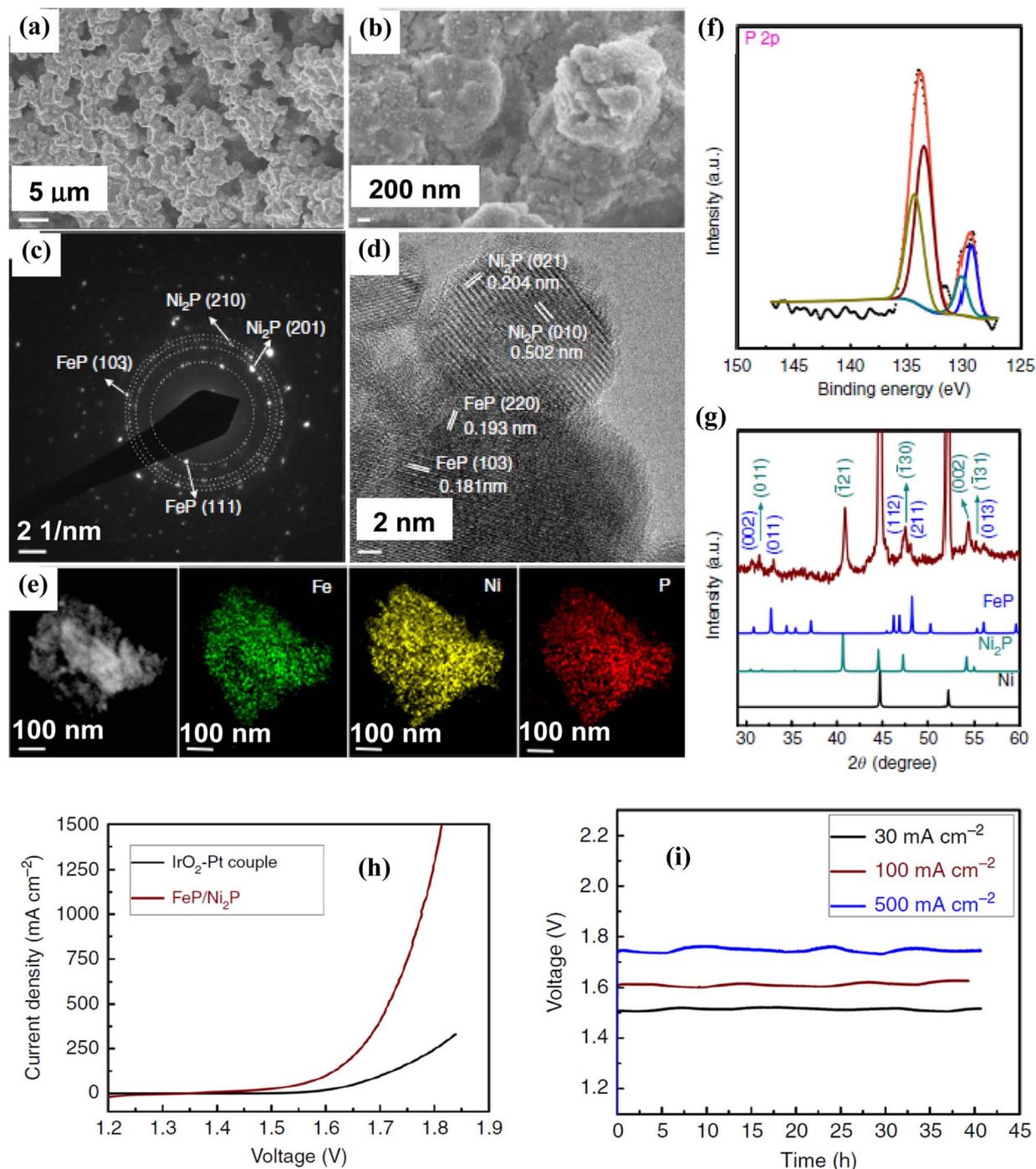


Fig. 4 Characterization of FeP/Ni<sub>2</sub>P: (a) and (b) SEM images; (c) SAED pattern; (d) HRTEM image; (e) TEM image and its corresponding EDX elemental mapping; (f) XPS spectrum; (g) XRD pattern; (h) LSV curves of FeP/Ni<sub>2</sub>P//FeP/Ni<sub>2</sub>P in comparison with IrO<sub>2</sub>/Pt for overall water splitting in 1 M KOH; (i) chronopotentiometric curves of FeP/Ni<sub>2</sub>P at 30, 100, and 500 mA cm<sup>-2</sup> in 1 M KOH (reproduced with permission from ref. 18 Copyright 2018, Nature Publishing Group).

In addition, Yu *et al.*<sup>86</sup> observed that Ni<sub>2(1-x)</sub>Mo<sub>2x</sub>P exhibits enhanced activity and stability for the HER. It was prepared on pretreated Ni foam by hydrothermal treatment followed by phosphorization at 500 °C for 1 h under an Ar atmosphere. Ni<sub>2(1-x)</sub>Mo<sub>2x</sub>P exhibits higher activity, higher electrochemical

surface area, and lower charge transfer resistance for the HER than Ni<sub>2</sub>P and NiMoO<sub>4</sub>. The XRD patterns show the prominent peaks for Ni<sub>2</sub>P and a tiny peak for the NiMoO<sub>4</sub> precursor. It contains Mo, Ni, and P, which are homogeneously distributed. In the high-resolution XPS spectra, the Ni 2p peak of



$\text{Ni}_{2(1-x)}\text{Mo}_{2x}\text{P}$  exhibits a slight negative shift when compared to that of  $\text{Ni}_2\text{P}$ , suggesting the modified electronic structure. It possesses highly porous nanowire array morphology. For the HER in 1 M KOH, it affords an  $\eta$  of  $-72$  mV at  $-10$  mA  $\text{cm}^{-2}$  and an  $\eta$  of  $-294$  mV at a current density of  $-1000$  mA  $\text{cm}^{-2}$ , suggesting its very high activity, while it affords reasonable stability for 160 h, suggesting its very high stability, and it undergoes negligible decay at  $-700$  mA  $\text{cm}^{-2}$  after 5000 cycles of CV, suggesting its high durability.

Besides, Yuan *et al.*<sup>87</sup> observed that  $\text{S-Co}_2\text{P@Ni}_2\text{P}$  exhibits enhanced activity and stability for the HER and OER. It was synthesized on cleaned Ti mesh by hydrothermal treatment followed by an ion-exchange process followed by a chemical deposition method followed by phosphidation at  $320$  °C for 2 h under an Ar atmosphere.  $\text{S-Co}_2\text{P@Ni}_2\text{P}$  exhibits higher activity for the HER and OER than  $\text{Co}_2\text{P@Ni}_2\text{P}$ . It is a S-doped  $\text{Co}_2\text{P@Ni}_2\text{P}$  heterostructure, where the  $\text{Co}_2\text{P}$  nanowire is the core, and the  $\text{Ni}_2\text{P}$  nanosheets are the shell. It exhibits a heterointerface between the  $\text{Co}_2\text{P}$  and  $\text{Ni}_2\text{P}$  phases. In the high-resolution XPS spectra, the Ni 2p and Co 2p peaks of  $\text{S-Co}_2\text{P@Ni}_2\text{P}$  exhibit slight shift when compared to that of  $\text{Co}_2\text{P@Ni}_2\text{P}$ , suggesting a modified electronic structure possibly due to the partial transfer of electrons from  $\text{Co}_2\text{P}$  to  $\text{Ni}_2\text{P}$  after S doping, which could be due to the higher electronegativity of Ni, when compared to that of Co. From the ultraviolet photoelectron spectroscopy, the value of the work function for  $\text{S-Co}_2\text{P}$  is 4.03 eV, which is lower than that of 4.78 eV for  $\text{Ni}_2\text{P}$ , suggesting the existence of a heterostructure, which could cause interfacial electron redistribution till the work functions reach equilibrium on both sides. For the OER in 1 M KOH, it undergoes negligible decay at  $600$  mA  $\text{cm}^{-2}$  after 1000 cycles of CV, suggesting its high durability. For the HER in 1 M KOH, it affords an  $\eta$  of  $-43$  mV at  $-10$  mA  $\text{cm}^{-2}$ , suggesting its very high activity, and it undergoes negligible decay at  $-700$  mA  $\text{cm}^{-2}$  after 1000 cycles of CV, suggesting its high durability. For overall water splitting in 1 M KOH,  $\text{S-Co}_2\text{P@Ni}_2\text{P}/\text{S-Co}_2\text{P@Ni}_2\text{P}$  affords a potential of 1.52 V at  $10$  mA  $\text{cm}^{-2}$ , suggesting its very high activity.

Active sites of nickel phosphide can be tuned by pulse-reverse electrodeposition, which could enhance the performance of the HER and OER. Kim *et al.*<sup>88</sup> observed that the NiP film exhibits enhanced activity and stability for the HER and OER. It was prepared by pulse-reverse electrodeposition, where the dissolution step can modulate the chemical states of P in the NiP film. The enhanced activity for the HER of NiP film can be achieved by enhancing the generation of  $\text{Ni}_x\text{P}$  by inhibiting the oxidation of P to  $\text{PO}_x^-$  in the pulse-reverse electrodeposition, the dissolution step should be as minimal as possible. On the other hand, the enhanced activity for the OER of the NiP film can be achieved by increasing the dissolution amount in the pulse-reverse electrodeposition.

Phosphorus doping can play a crucial role in the formation of a nanoporous surface, where the nanoporous surface can be formed by the electrochemical etching of a phosphorus-doped alloy, which could expose abundant active sites and that could

improve the performance of the HER and OER. Feng *et al.*<sup>89</sup> observed that e-FeCoNiCu-P exhibits enhanced activity and stability for the HER and OER, where e-FeCoNiCu-P is electrochemically etched FeCoNiCu-P. The following steps were involved in its preparation: first, FeCoNiCu foil as a medium entropy alloy was obtained by the arc melting process. Then, FeCoNiCu-P was obtained by phosphidation of the pretreated FeCoNiCu foil. Finally, e-FeCoNiCu-P was prepared by electrochemical etching of FeCoNiCu-P. e-FeCoNiCu-P exhibits higher activity for the HER and OER than FeCoNiCu-P. It possesses a nanoporous surface, which could expose abundant active sites and enhance the performance of the HER and OER.

Besides, Li *et al.*<sup>90</sup> observed that  $\text{Ni}_5\text{P}_4@\text{FeP}$  exhibits enhanced activity and stability for the OER. It was obtained on Ni foam by immersion for about 5 s (corrosion process) followed by phosphorization at  $350$  °C for 1 h under an  $\text{N}_2$  atmosphere.  $\text{Ni}_5\text{P}_4@\text{FeP}$  exhibits higher activity and lower charge transfer resistance for the OER than  $\text{Ni}_5\text{P}_4$  and FeP. It is crystalline, while it exhibits a heterointerface between  $\text{Ni}_5\text{P}_4$  and FeP phases. It possesses nanosheet array morphology. It is reconstructed into  $\text{NiFe}_2\text{O}_4$  during the OER at low oxidation potentials, while  $\text{NiFe}_2\text{O}_4$  is partially reconstructed into Ni/FeOOH at large oxidation potentials. Thus,  $\text{Ni}_5\text{P}_4@\text{FeP}$  is reconstructed into Ni/FeOOH@ $\text{NiFe}_2\text{O}_4$  during the OER, where this genuinely active species has high structural reversibility. For the OER in 1 M KOH, it affords an  $\eta$  of 205 mV at  $10$  mA  $\text{cm}^{-2}$ , suggesting its very high activity. In contrast, it undergoes negligible decay at  $100$  mA  $\text{cm}^{-2}$  for 100 h, suggesting its very high stability.

Fabricating nanostructured phosphide-based electrocatalysts using relatively low-cost metals such as Fe, Mn, and Zn is highly desirable for green synthesis, which could modify the electronic structure, provide optimal adsorption energy with intermediates, facilitate the gas evolution, and that could enhance the performance for the HER and OER. Huang *et al.*<sup>28</sup> observed that Zn-Fe/Mn@Mn-FeP exhibits enhanced activity and stability for the HER and OER. It was prepared by the etching of  $\text{Fe}_{70}\text{Mn}_{28}\text{Zn}_2$  for 1 h followed by annealing at  $400$  °C for 1 h in air followed by etching for 1 h followed by phosphorization at  $500$  °C for 3 h in an Ar atmosphere. Zn-Fe/Mn@Mn-FeP exhibits higher activity and electrochemical surface area for the HER than Fe/Mn@Mn-FeP, Zn-Fe@Zn-FeP, and Fe@FeP. Zn-Fe/Mn@Mn-FeP exhibits higher activity for the OER than Fe/Mn@Mn-FeP, Zn-Fe@Zn-FeP, and Fe@FeP. It is Zn-Fe/Mn@Mn-FeP. It contains orthorhombic FeP, cubic Fe, and Mn, where the Zn phase is not observed, possibly due to its low content. It contains an Mn-P bond. In the high-resolution XPS spectra, the Fe 2p peak of Zn-Fe/Mn@Mn-FeP exhibits a slight positive shift when compared to that of metallic Fe, and the Mn 2p peak of Zn-Fe/Mn@Mn-FeP exhibits a slight positive shift, when compared to that of metallic Mn, suggesting a modified electronic structure. It contains Mn, Zn, Fe, and P, which are homogeneously distributed. It possesses ultrathin nanosheet morphology. For the HER in 1 M KOH, it affords an  $\eta$  of



–165 mV at  $-10 \text{ mA cm}^{-2}$ , suggesting its very high activity. S-doped NiFeP can be derived from the phosphorization of MOF, and that could modify the electronic structure, provide optimal adsorption energy with intermediates, downshift the d-band center from the Fermi level, which could enhance the performance for the HER and OER. Li *et al.*<sup>91</sup> observed that S-NiFeP-20 exhibits enhanced activity and stability for the HER, while S-NiFeP-10 exhibits enhanced activity and stability for the OER. S-NiFeP-20 or S-NiFeP-10 was prepared on pretreated carbon cloth by hydrothermal treatment (for MOF preparation) followed by phosphorization at 300 °C for 2 h under an Ar atmosphere. It is S-doped NiFeP. In the high-resolution XPS spectra, the Fe 2p peak of S-NiFeP exhibits a slight positive shift compared to NiFeP, suggesting a modified electronic structure due to S doping. The DFT calculations disclose that the S doping in NiFeP plays a crucial role in the formation of optimal  $\Delta G$  values for the formation of intermediates on Ni atoms, and that enhances the performance of the OER. S-NiFeP-20 downshifts the d-band center from the Fermi level, and that enhances the performance for the HER. In 1 M KOH, S-NiFeP-20 affords an  $\eta$  of  $-56 \text{ mV}$  at  $-10 \text{ mA cm}^{-2}$  for the HER, while S-NiFeP-10 affords an  $\eta$  of 201 mV at  $10 \text{ mA cm}^{-2}$  for the OER, suggesting their very high activity. For overall water splitting in 1 M KOH, S-NiFeP-10<sup>OER</sup>/S-NiFeP-20<sup>HER</sup> affords a potential of 1.5 V at  $10 \text{ mA cm}^{-2}$ , suggesting its very high activity.

Besides, Kumar *et al.*<sup>13</sup> observed that the NiP<sub>2</sub>-FeP<sub>2</sub>@Cu nanoarray exhibits enhanced activity and stability for the HER. The following steps were involved in its preparation: at first, a Cu nanoarray was grown on pretreated Cu foam by chemical oxidation followed by calcination followed by electrochemical reduction. Then, NiFe LDH was grown on the Cu nanoarray by electrodeposition. Finally, the NiP<sub>2</sub>-FeP<sub>2</sub>@Cu nanoarray was obtained by the phosphidation of the NiFe LDH@Cu nanoarray at 350 °C for 2 h under an Ar atmosphere. The NiP<sub>2</sub>-FeP<sub>2</sub>@Cu nanoarray on Cu foam exhibits higher activity, higher electrochemical surface area, and lower charge transfer resistance for the HER than NiP<sub>2</sub>-FeP<sub>2</sub> on carbon fiber paper. It is NiP<sub>2</sub>-FeP<sub>2</sub> on a Cu nanoarray. It exhibits heterointerfaces between NiP<sub>2</sub> and FeP<sub>2</sub> phases. It contains Ni, Fe, P, and Cu, which are homogeneously distributed. The high-resolution XPS spectra of Cu 2p for the NiP<sub>2</sub>-FeP<sub>2</sub>@Cu nanoarray obtained before and after Ar etching disclose the existence of Cu<sup>0</sup> along with a small peak, where the small peak is attributed to Cu<sup>δ+</sup>, which could be due to the coupling between NiP<sub>2</sub>-FeP<sub>2</sub> and the Cu nanoarray. For the HER in 1 M KOH, it affords an  $\eta$  of  $-23.6 \text{ mV}$  at  $-10 \text{ mA cm}^{-2}$  and an  $\eta$  of  $-357 \text{ mV}$  at a current density of  $-1000 \text{ mA cm}^{-2}$ , suggesting its substantially very high activity, while it affords reasonable stability at  $-1000 \text{ mA cm}^{-2}$  for 50 h, suggesting its very high stability.

Moreover, Zhang *et al.*<sup>92</sup> observed that Ni<sub>2</sub>P/NC exhibits enhanced activity and stability for the HER. It was synthesized by a coordination reaction followed by calcination followed by phosphorization followed by etching. Ni<sub>2</sub>P/NC exhibits higher activity for the HER than Ni<sub>2</sub>P. It is composed of nickel

phosphide nanoparticles, which are anchored on N-doped porous carbon nanorods. It contains N, C, Ni, and P, which are homogeneously distributed. In the high-resolution XPS spectra, the Ni 2p peak of Ni<sub>2</sub>P/NC exhibits a slight positive shift compared to that of Ni<sub>2</sub>P, suggesting a modified electronic structure, possibly due to the partial transfer of electrons between Ni<sub>2</sub>P and NC. It possesses nanorod morphology, having abundant mesopores.

In addition, Liu *et al.*<sup>93</sup> observed that NiCoFe-P/C exhibits enhanced activity and stability for the HER and OER. It was synthesized on pretreated Ni foam by hydrothermal treatment followed by carbonization at 450 °C for 2 h in N<sub>2</sub> followed by phosphorization at 350 °C for 2 h in N<sub>2</sub>. NiCoFe-P/C exhibits higher activity and electrochemical surface area for the HER than NiCoFe-ZIF and NiCoFe-C. NiCoFe-P/C exhibits higher activity for the OER than NiCoFe-ZIF and NiCoFe-C. It is composed of 0D NiCoFe-P quantum dots, which are anchored on 2D porous carbon, where NiCoFe-P comprises Ni<sub>2</sub>P, CoP, and Fe<sub>2</sub>P phases. It exhibits heterointerfaces. In the high-resolution XPS spectra, the Ni 2p peak of NiCoFe-P/C is slightly less than that of Ni<sup>2+</sup>, suggesting a modified electronic structure. For the HER in 1 M KOH, it affords an  $\eta$  of  $-87 \text{ mV}$  at  $-10 \text{ mA cm}^{-2}$ , suggesting its very high activity. For overall water splitting in 1 M KOH, NiCoFe-P/C//NiCoFe-P/C affords a potential of 1.55 V at  $10 \text{ mA cm}^{-2}$ , suggesting its very high activity. The surface properties of the materials can be improved by plasma treatment.<sup>94</sup> Fabrication of Co-Nb bimetallic phosphide on plasma-modified carbon cloth could modify the electronic structure, provide optimal adsorption energy with intermediates, enhance the conductivity, and that could enhance the performance for the HER. Xiang *et al.*<sup>95</sup> observed that CoP<sub>3</sub>-Nb<sub>2</sub>P/PCC exhibits enhanced activity and stability for the HER (PCC: plasma modified carbon cloth). The following steps were involved in its preparation: first, plasma-modified carbon-cloth was obtained by dielectric barrier discharge atmospheric pressure plasma treatment on cleaned carbon cloth. Then, the CoO-NbO/PCC was prepared by hydrothermal treatment. Finally, CoP<sub>3</sub>-Nb<sub>2</sub>P/PCC was obtained by phosphorization at 550 °C for 2 h in N<sub>2</sub>. CoP<sub>3</sub>-Nb<sub>2</sub>P/PCC exhibits higher activity, higher electrochemical surface area, and lower charge transfer resistance for the HER than CoO-NbO/PCC. It comprises the cubic phase of CoP<sub>3</sub> and the orthorhombic phase of Nb<sub>2</sub>P on plasma-modified carbon cloth. It contains Nb, Co, and P, which are homogeneously distributed. It possesses drum-like morphology. DFT calculations and *in situ* Raman spectra results disclose that the enhanced performance for the HER of CoP<sub>3</sub>-Nb<sub>2</sub>P/PCC is attributed to the synergistic effect between Nb and Co phosphide. For the HER in 1 M KOH, it affords an  $\eta$  of  $-111 \text{ mV}$  at  $-10 \text{ mA cm}^{-2}$  and an  $\eta$  of  $-375 \text{ mV}$  at a current density of  $-1000 \text{ mA cm}^{-2}$ , suggesting its very high activity, and it undergoes negligible decay at  $-500 \text{ mA cm}^{-2}$  after 5000 cycles of CV, suggesting its high durability.

Besides, Bai *et al.*<sup>6e</sup> observed that Fe<sub>2</sub>P/Co@NPC exhibits enhanced activity and stability for the HER and OER. It was



synthesized by hydrothermal treatment followed by carbonization at 950 °C for 3 h under an Ar atmosphere. Fe<sub>2</sub>P/Co@NPC exhibits higher activity and lower charge transfer resistance for the HER and OER than Co@NC and Fe<sub>2</sub>P@NPC. It is composed of Fe<sub>2</sub>P and Co nanoparticles, which are embedded in P and N-incorporated porous carbon. It contains Fe, Co, C, N, and P, which are homogeneously distributed. It contains pyridinic N, pyrrolic N, and graphitic N. It contains micropores and mesopores. It exhibits a high specific surface area of 547 m<sup>2</sup> g<sup>-1</sup>.

Moreover, Singh *et al.*<sup>96</sup> observed that NiP<sub>2</sub>/NbP@CNTs exhibit enhanced activity and stability for the HER and OER (CNTs: carbon nanotubes). It was obtained on Ni foam by electrodeposition followed by chemical vapor deposition followed by hydrothermal treatment followed by phosphorization at 300 °C for 2 h under an Ar atmosphere. NiP<sub>2</sub>/NbP@CNTs exhibit higher activity and electrochemical surface area for the HER and OER than NbP@CNTs and NiP<sub>2</sub>@CNTs. It comprises carbon nanotubes as the core and NiP<sub>2</sub>/NbP nanosheets as the shell, while it also contains a small amount of Nb<sub>2</sub>Ni<sub>9</sub>P phase. It exhibits a heterointerface between the NbP and NiP<sub>2</sub> phases. In the high-resolution XPS spectra, the Ni 2p peak of NiP<sub>2</sub>/NbP@CNTs exhibits a slight negative shift when compared to that of NiP<sub>2</sub>@CNTs, the Nb 3d peak of NiP<sub>2</sub>/NbP@CNTs exhibits a slight positive shift, when compared to that of pure NbP, suggesting a modified electronic structure, possibly due to the partial transfer of electrons from Ni to Nb, which could be due to the higher electronegativity of Ni, when compared to that of Nb. For overall water splitting in 1 M KOH, NiP<sub>2</sub>/NbP@CNTs//NiP<sub>2</sub>/NbP@CNTs affords a potential of 1.51 V at 10 mA cm<sup>-2</sup>, suggesting its very high activity.

In addition, Chu *et al.*<sup>97</sup> observed that Ni-CoP/Co<sub>2</sub>P@NC exhibits enhanced activity and stability for the HER, while the activated Ni-CoP/Co<sub>2</sub>P@NC exhibits enhanced activity and stability for the OER. Ni-CoP/Co<sub>2</sub>P@NC was prepared by epitaxial growth followed by pyrolysis. The activated Ni-CoP/Co<sub>2</sub>P@NC was obtained by electrochemical activation of Ni-CoP/Co<sub>2</sub>P@NC, where the activation forms the thin cobalt oxyhydroxide layer as the active species for the OER on the surface of Ni-CoP/Co<sub>2</sub>P@NC. Ni-CoP/Co<sub>2</sub>P@NC exhibits higher activity and lower charge transfer resistance for the HER than CoP/Co<sub>2</sub>P@NC. In comparison, the activated Ni-CoP/Co<sub>2</sub>P@NC exhibits higher activity and lower charge transfer resistance for the OER than Ni-CoP/Co<sub>2</sub>P@NC and CoP/Co<sub>2</sub>P@NC. Ni-CoP/Co<sub>2</sub>P@NC exhibits numerous interfaces along with defects between the 2D nanosheets and 3D nanoparticles. It contains Co<sub>2</sub>P and CoP phases. Graphitized carbon layers cover the cobalt phosphides. In the high-resolution XPS spectra, the Co 2p peak of Ni-CoP/Co<sub>2</sub>P@NC exhibits a slight negative shift compared to that of CoP/Co<sub>2</sub>P@NC, suggesting a modified electronic structure. It contains Ni, Co, C, P, O, and N, which are homogeneously distributed. For overall water splitting in 1 M KOH, the activated-Ni-CoP/Co<sub>2</sub>P@NC<sup>OER</sup>//Ni-CoP/Co<sub>2</sub>P@NC<sup>HER</sup> affords a potential of 1.59 V at 10 mA cm<sup>-2</sup>, suggesting its very

high activity. In contrast, it undergoes negligible decay at 1.6 V for 400 h, suggesting its very high stability.

Besides, Riyajuddin *et al.*<sup>12</sup> observed that Gr-CNTs-Sn<sub>4</sub>P<sub>3</sub> exhibit enhanced activity and stability for overall water splitting (Gr: graphene; CNTs: carbon nanotubes). It was prepared on pretreated Ni foam by thermal chemical vapor deposition followed by immersion in ferric nitrate solution for 12 h followed by thermal chemical vapor deposition followed by electrochemical deposition followed by phosphorization through solvothermal treatment followed by acid treatment. Gr-CNTs-Sn<sub>4</sub>P<sub>3</sub> exhibits higher activity for the OER than Gr-CNTs. It is composed of Sn<sub>4</sub>P<sub>3</sub> with a rhombohedral structure, which is grown on a carbon matrix, where the carbon matrix is composed of graphene and multi-walled carbon nanotubes. It exhibits a heterojunction interface between CNTs and Sn<sub>4</sub>P<sub>3</sub>. In the high-resolution XPS spectra, the C 1s peak of Gr-CNTs-Sn<sub>4</sub>P<sub>3</sub> exhibits a slight positive shift when compared to that of Gr-CNTs, suggesting a modified electronic structure, possibly due to the partial transfer of electrons between the carbon matrix and Sn<sub>4</sub>P<sub>3</sub>. It possesses a flower-like morphology. It exhibits a superhydrophilic surface with a contact angle of 0°, suggesting its high surface wettability. For the OER in 1 M KOH, it affords an η of 169 mV at 20 mA cm<sup>-2</sup>, suggesting its very high activity, while it affords ~96% retention for 105 h, suggesting its very high stability, and it undergoes negligible decay at 200 mA cm<sup>-2</sup> after 5000 cycles of CV, suggesting its high durability. For overall water splitting in 1 M KOH, Gr-CNTs-Sn<sub>4</sub>P<sub>3</sub>//Gr-CNTs-Sn<sub>4</sub>P<sub>3</sub> affords a potential of 1.482 V at 10 mA cm<sup>-2</sup>, suggesting its very high activity.

Moreover, Vijayakumar *et al.*<sup>98</sup> observed that CoP-NC@NiFeP exhibits enhanced activity and stability for the HER and OER. It was prepared by precipitation followed by carbonization followed by pyro-phosphatization followed by hydrothermal treatment followed by pyro-phosphatization. CoP-NC@NiFeP exhibits higher activity for the HER and OER than CoP-NC and Co<sub>3</sub>O<sub>4</sub>-NC. It is composed of CoP-NC as a core and NiFeP as a shell. It contains crystalline CoP and NiFeP phases, while it contains N-doped amorphous carbon. It contains graphitic N, pyridinic N, and pyrrolic N. It contains Co, Ni, Fe, C, N, P, and O, which are homogeneously distributed. It possesses a coral-like morphology.

Co<sub>x</sub>P/NC can be obtained from melamine-modified ZIF-9, while the surface modification of ZIF-9 with melamine can generate robust Co coordination sites on the surface of the ZIF-9 by coordination of Co with N donor sites in the melamine, and that could enhance the performance of the OER (ZIF-9: cobalt benzimidazole zeolitic imidazolate framework). Liu *et al.*<sup>99</sup> observed that Co<sub>x</sub>P/NC-melamine exhibits enhanced activity and stability for the OER. The following steps are involved in its preparation. First, ZIF-9 was obtained by the microwave hydrothermal treatment. Then, ZIF-9-melamine was prepared by modifying ZIF-9 with melamine at 100 °C for 1 h. Finally, Co<sub>x</sub>P/NC-melamine was obtained by phosphidation at 700 °C for 2 h under an Ar atmosphere. The surface engineering of ZIF-



9 using melamine constructs robust Co coordination sites on the surface of the ZIF-9 *via* coordination of Co with N donor sites in the melamine. DFT calculations disclose that the ZIF-9 is surface modified using melamine at coordinatively unsaturated Co sites and at coordinatively saturated Co sites through a thermodynamically favored ligand exchange process between melamine and benzimidazole in ZIF-9. Co<sub>x</sub>P/NC prepared using melamine exhibits higher activity and electrochemical surface area for the OER than Co<sub>x</sub>P/NC prepared using hexamethylenetetramine, Co<sub>x</sub>P/NC prepared using phenanthroline, and Co<sub>x</sub>P/NC. It is composed of Co<sub>x</sub>P nanoparticles, which are dispersed on the carbon rods. It contains Co<sub>2</sub>P and CoP phases. It contains graphitic N, pyridinic N, Co–N<sub>x</sub>, and pyrrolic N. It contains Co, P, N, and C, which are homogeneously distributed.

Developing a synthesis route at an industrial scale for efficient electrocatalysts for the HER and OER is highly desirable for industrial applications. Hundred-gram scale production of the Cu<sub>3</sub>P–Cu<sub>2</sub>O heterostructure integrated with N, P dual doped porous carbon can be achieved by carbonization of Cu<sup>2+</sup>-

containing ion-exchange resins with KOH, and that could modify the electronic structure and provide abundant active sites, which could enhance the performance for the HER and OER. Zhu *et al.*<sup>100</sup> observed that Cu<sub>3</sub>P–Cu<sub>2</sub>O/NPC exhibits enhanced activity and stability for the HER and OER. Hundred-gram scale production of Cu<sub>3</sub>P–Cu<sub>2</sub>O/NPC was achieved by carbonization of Cu<sup>2+</sup>-containing ion-exchange resins with KOH, where the pyrolysis was performed for 1 h at 850 °C under an N<sub>2</sub> atmosphere. Cu<sub>3</sub>P–Cu<sub>2</sub>O/NPC exhibits higher activity for the HER and OER than Cu<sub>2</sub>O/NPC and Cu<sub>3</sub>P/NPC. Cu<sub>3</sub>P–Cu<sub>2</sub>O/NPC exhibits lower charge transfer resistance for the OER than Cu<sub>2</sub>O/NPC and Cu<sub>3</sub>P/NPC. It is composed of Cu<sub>3</sub>P–Cu<sub>2</sub>O nanoparticles, which are embedded in N,P dual-doped porous carbon. It exhibits a heterointerface between hexagonal Cu<sub>3</sub>P and cubic Cu<sub>2</sub>O. It contains quaternary N, pyridinic N, and pyrrolic N. For the OER in 1 M KOH, it affords an  $\eta$  of 286 mV at 10 mA cm<sup>-2</sup>, suggesting its very high activity, and it undergoes negligible decay at 150 mA cm<sup>-2</sup> after 20 000 cycles of CV, suggesting its high durability. For the HER in 1 M KOH, it

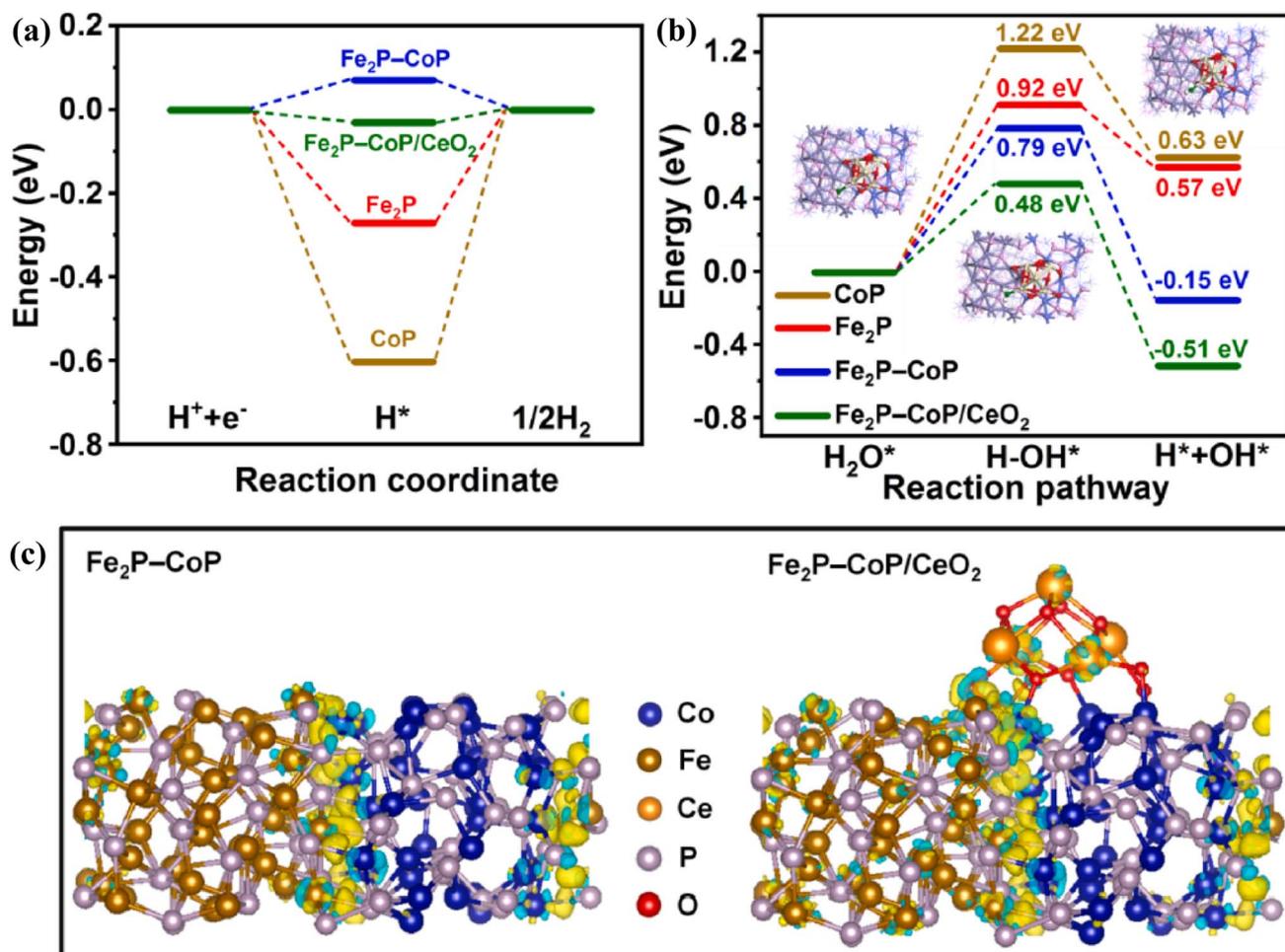


Fig. 5 (a) Gibbs free energy profiles for the HER on Fe<sub>2</sub>P–CoP/CeO<sub>2</sub> in comparison with Fe<sub>2</sub>P, CoP, and Fe<sub>2</sub>P–CoP; (b) water dissociation capability of Fe<sub>2</sub>P–CoP/CeO<sub>2</sub> in comparison with Fe<sub>2</sub>P, CoP, and Fe<sub>2</sub>P–CoP (insets depict the final, transient, and initial state geometries of Fe<sub>2</sub>P–CoP/CeO<sub>2</sub> for water dissociation); (c) charge density difference plot of Fe<sub>2</sub>P–CoP/CeO<sub>2</sub> in comparison with Fe<sub>2</sub>P–CoP, where the yellow color indicates electron accumulation, and the cyan color represents electron depletion (reproduced with permission from ref. 101 Copyright 2022, Elsevier B.V.).



affords an  $\eta$  of  $\sim -155$  mV at  $-10$  mA cm $^{-2}$ , suggesting its very high activity, and it undergoes negligible decay at  $-45$  mA cm $^{-2}$  after 20 000 cycles of CV, suggesting its high durability. For overall water splitting in 1 M KOH, Cu $_3$ P-Cu $_2$ O/NPC//Cu $_3$ P-Cu $_2$ O/NPC affords a potential of 1.57 V at 10 mA cm $^{-2}$ , suggesting its very high activity, while it affords 98.19% retention at 1.7 V for 168 h, suggesting its very high stability.

Besides, Ding *et al.*<sup>101</sup> observed that Fe $_2$ P-CoP/CeO $_2$  exhibits enhanced activity and stability for the HER and OER. It was synthesized by co-precipitation followed by refluxing followed by phosphidation (300 °C for 2 h under an N $_2$  atmosphere). Fe $_2$ P-CoP/CeO $_2$  exhibits higher activity and electrochemical surface area for the HER and OER than Fe $_2$ P-CoP and CeO $_2$ . It contains a higher amount of oxygen vacancies than Fe $_2$ P-CoP. It is crystalline and contains Fe $_2$ P, CoP, and CeO $_2$  phases. It contains a triphase heterojunction. It contains Co, Fe, P, O, and Ce, which are homogeneously distributed. It possesses a porous nanocube structure having mesopores and micropores. In the high-resolution XPS spectra, the peaks corresponding to the Fe-P bond and Co-P bond of Fe $_2$ P-CoP/CeO $_2$  show a slight positive shift when compared to that of Fe $_2$ P-CoP, while the peaks of Ce 3d in Fe $_2$ P-CoP/CeO $_2$  show a slight negative shift when compared to that of CeO $_2$ , suggesting the modified electronic structure and strong electronic interaction at the triphase heterojunction, where the partial electrons could be transferred between Co/Fe and Ce. The  $\Delta G_{H^*}$  value of Fe $_2$ P-CoP/CeO $_2$  was calculated to be  $-0.03$  eV (Fig. 5a), suggesting its enhanced intrinsic HER catalytic activity. The water dissociation energy of Fe $_2$ P-CoP/CeO $_2$  (0.48 eV) is lower than that of CoP, Fe $_2$ P, and Fe $_2$ P-CoP (Fig. 5b), suggesting its accelerated HER kinetics. As shown in Fig. 5c, the charge density difference of Fe $_2$ P-CoP and Fe $_2$ P-CoP/CeO $_2$  discloses the increase in localized charge density at the Fe $_2$ P-CoP interface, suggesting the strong interaction of Fe $_2$ P with CoP. In contrast, charge density has been redistributed at the three-phase heterojunction interface, possibly due to the introduction of CeO $_2$  with Fe $_2$ P-CoP, suggesting the enhanced intrinsic electrocatalytic activity. For the HER in 1 M KOH, it affords an  $\eta$  of  $-45$  mV at  $-10$  mA cm $^{-2}$ , suggesting its outstanding activity. For overall water splitting in 1 M KOH, Fe $_2$ P-CoP/CeO $_2$ //Fe $_2$ P-CoP/CeO $_2$  affords a potential of 1.52 V at 10 mA cm $^{-2}$ , suggesting its very high activity, while it affords reasonable stability at 500 mA cm $^{-2}$  for 40 h, suggesting its very high stability.

Moreover, Peng *et al.*<sup>102</sup> observed that Fe $_2$ P-WO $_{2.92}$  exhibits enhanced activity and stability for the OER. It was synthesized on pretreated Ni foam with hydrothermal treatment, followed by phosphating at 350 °C for 2 h under an N $_2$  atmosphere. Fe $_2$ P-WO $_{2.92}$  exhibits higher activity and electrochemical surface area for the OER than Fe $_2$ P and WO $_{2.92}$ . It is composed of monoclinic WO $_{2.92}$  and hexagonal Fe $_2$ P phases. It contains oxygen vacancies. It contains W, Fe, P, C, and O, which are homogeneously distributed. It possesses a porous structure. For the OER in 1 M KOH, it affords an  $\eta$  of 215 mV at 10 mA cm $^{-2}$ , suggesting its

very high activity, while it affords 93% retention at 100 mA cm $^{-2}$  for 60 h, suggesting its very high stability.

In addition, Chen *et al.*<sup>103</sup> observed that Co(OH) $_2$ /NiP $_x$  exhibits enhanced activity and stability for the OER. It was prepared on a cleaned carbon cloth by a two-step electrodeposition approach. Co(OH) $_2$ /NiP $_x$  exhibits higher activity and electrochemical surface area for the OER than NiP $_x$  and Co(OH) $_2$ . It is composed of Co(OH) $_2$  and NiP $_x$ . In the high-resolution XPS spectra, the Co 2p peak of Co(OH) $_2$ /NiP $_x$  exhibits a slight shift compared to that of Co(OH) $_2$ , suggesting a modified electronic structure. It possesses nanosheet array morphology. It exhibits a highly hydrophilic surface with a contact angle of 18.9°, suggesting its high surface wettability.

Besides, Cheng *et al.*<sup>104</sup> observed that CoP/FeOOH exhibits enhanced activity and stability for the OER. The following steps were involved in its preparation: at first, Co $_3$ O $_4$  nanofibers were synthesized by electrospinning, followed by calcination, followed by annealing. Then, CoP was obtained by phosphorization of Co $_3$ O $_4$  for 2 h at 400 °C under an Ar atmosphere. Finally, CoP/FeOOH was prepared by stirring the CoP in ethanol with FeCl $_3$  and NH $_4$ HCO $_3$  for 6h at room temperature. CoP/FeOOH exhibits higher activity, higher electrochemical surface area, and lower charge transfer resistance for the OER than CoP and FeOOH. It is composed of a thin amorphous FeOOH layer, which is covered on CoP porous nanofiber. It exhibits a hetero-interface between CoP and FeOOH. In the high-resolution XPS spectra, the Co 2p peak of CoP/FeOOH exhibits a slight shift compared to that of CoP, suggesting a modified electronic structure.

Fabrication of a nickel phosphate microprism with unique nanochannels through a one-step solvothermal method could expose more active sites, enhancing HER performance. Calcinating the nickel phosphate microprism followed by incorporating Fe could increase the proportion of high valence Ni ions, modify the electronic structure, and enhance the performance of the OER. Zhao *et al.*<sup>105</sup> observed that VSB/NiPO exhibits enhanced activity and stability for the HER, while Fe-VSB/NiPO-500 exhibits enhanced activity and stability for the OER. VSB/NiPO is a nickel phosphate microprism. The microprism is mainly composed of Versailles-Santa Barbara-5, which is a kind of nickel phosphate molecular sieve having the chemical formula of Ni $_{20}$ [(OH) $_{12}$ (H $_2$ O) $_6$ ][(HPO $_4$ ) $_8$ (PO $_4$ ) $_4$ ] $\cdot$ 12H $_2$ O. VSB/NiPO possesses unique nanochannels, which could expose more active sites and that could enhance the performance for the HER. VSB/NiPO exhibits higher activity, higher electrochemical surface area, and lower charge transfer resistance for the HER than Ni(OH) $_2$  and Ni(PO $_3$ ) $_2$ . VSB/NiPO was prepared on the pretreated Ni foam by a solvothermal method. VSB/NiPO-500 was obtained by the calcination of VSB/NiPO at 500 °C. Fe-VSB/NiPO-500 was prepared by immersing VSB/NiPO-500 in Fe(NO $_3$ ) $_3$  solution at room temperature for 5 min. In the high-resolution XPS spectra, the proportion of Ni $^{3+}$  in Fe-VSB/NiPO-500 is 92.86%, which is much higher than that of VSB/NiPO (59.52%), suggesting the modified electronic structure after Fe



doping, which could be due to the partial transfer of electrons between Fe and VSB/NiPO-500. Fe-VSB/NiPO-500 with a higher proportion of high valence Ni ions and a modified electronic structure could enhance the performance of the OER. Fe-VSB/NiPO-500 exhibits higher activity, higher electrochemical surface area, and lower charge transfer resistance for the OER than VSB/NiPO-500. For the OER in 1 M KOH, Fe-VSB/NiPO-500 affords an  $\eta$  of  $\sim 227$  mV at  $50 \text{ mA cm}^{-2}$ , suggesting its very high activity, while it affords 98.2% retention at  $50 \text{ mA cm}^{-2}$  for 100 h, suggesting its very high stability. For the HER in 1 M KOH, it affords an  $\eta$  of  $-58$  mV at  $-10 \text{ mA cm}^{-2}$ , suggesting its very high activity. For overall water splitting in 1 M KOH, Fe-VSB/NiPO-500<sup>OER</sup>//VSB/NiPO<sup>HER</sup> affords a potential of 1.487 V at  $10 \text{ mA cm}^{-2}$ , suggesting its very high activity. In contrast, it affords 96.44% retention at  $100 \text{ mA cm}^{-2}$  for 100 h, suggesting its very high stability.

#### 2.4. Constructing nitride electrocatalysts

Cobalt nitride coupled with N-doped carbon with a porous nanostructure could modify the electronic structure, afford optimal adsorption energy with intermediates, increase the conductivity, and that could enhance the performance of the HER and OER. Song *et al.*<sup>106</sup> observed that CoN@NC exhibits enhanced activity and stability for the HER and OER. The following steps were involved in its preparation: at first, the Co

precursor was obtained on cleaned Ni foam by a vaporization deposition approach at  $70^\circ\text{C}$  for 1 h. Finally, CoN@NC was prepared by calcinating the Co precursor under an  $\text{NH}_3$  atmosphere at  $300^\circ\text{C}$  for 1 h. CoN@NC exhibits higher activity and lower charge transfer resistance for the HER and OER than the Co precursor. It is composed of crystalline CoN, which is wrapped by an amorphous N-doped carbon layer. It contains Co-N, pyrrolic-N, pyridinic-N, and graphitic-N. It contains Co, C, and N, which are homogeneously distributed. It contains defects. It possesses porous nanosheet morphology. It exhibits the formation of CoOOH as the active species during the OER, which could be due to the partial oxidation of CoN in CoN@NC. For the HER in 1 M KOH, it affords an  $\eta$  of  $-61$  mV at  $-10 \text{ mA cm}^{-2}$ , suggesting its very high activity. For overall water splitting in 1 M KOH, CoN@NC//CoN@NC affords a potential of 1.53 V at  $10 \text{ mA cm}^{-2}$ , suggesting its very high activity.

Fabrication of nanostructured antiperovskite nitrides could modify the electronic structure, enhance the conductivity, expose abundant active sites, and that could enhance the performance of the HER and OER. Zhu *et al.*<sup>107</sup> observed that  $\text{CoN}_{0.73}\text{Co}_3$  exhibits enhanced activity and stability for the HER, and  $\text{CuNC}_3$  exhibits enhanced activity and stability for the OER.  $\text{CoN}_{0.73}\text{Co}_3$  or  $\text{CuNC}_3$  was prepared by hydrothermal treatment followed by annealing at  $420^\circ\text{C}$  for 2 h under an  $\text{NH}_3$  atmosphere.  $\text{CoN}_{0.73}\text{Co}_3$  exhibits higher activity and lower

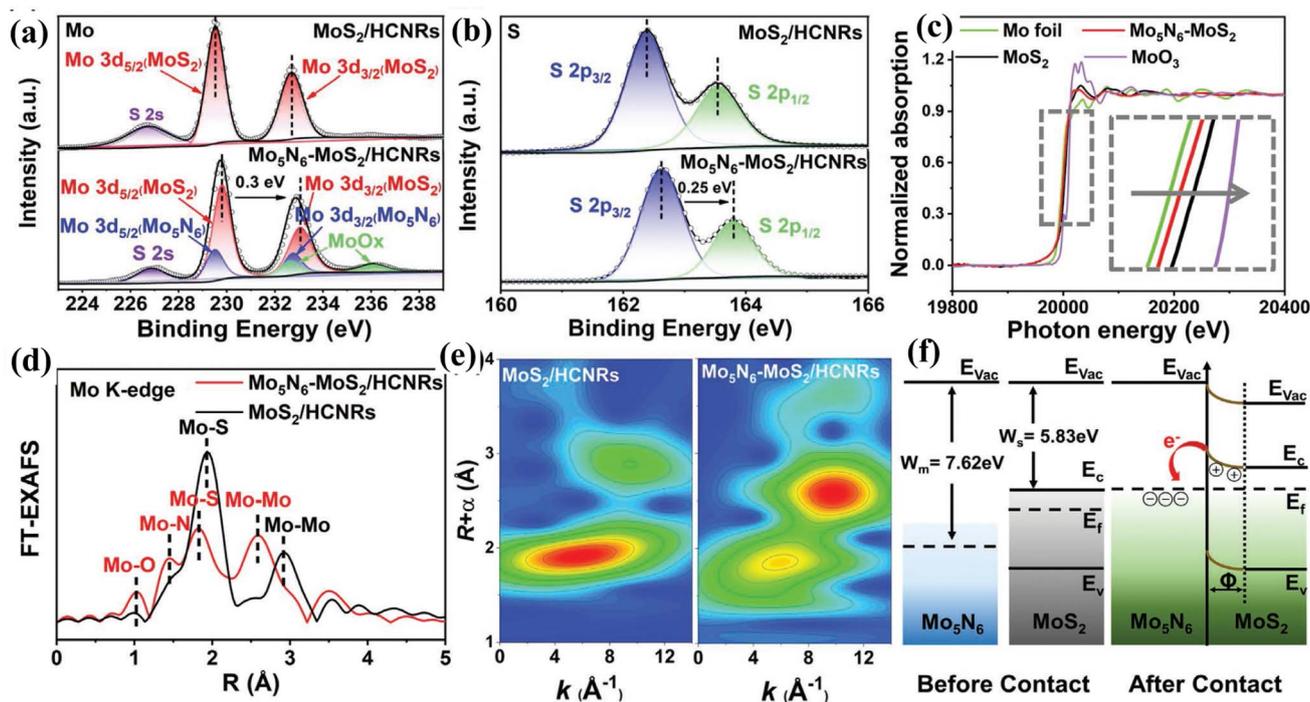


Fig. 6 High-resolution XPS spectra of (a) Mo 3d and (b) S 2p obtained from  $\text{Mo}_5\text{N}_6\text{-MoS}_2\text{-HCNRs}$  in comparison with  $2\text{H-MoS}_2\text{/HCNRs}$ ; (c) Mo K-edge XANES spectrum of  $\text{Mo}_5\text{N}_6\text{-MoS}_2\text{/HCNR}$  in comparison with Mo foil,  $\text{MoO}_3$ , and  $2\text{H-MoS}_2\text{/HCNRs}$ ; (d) FT-EXAFS curves and (e) WT-EXAFS of  $\text{Mo}_5\text{N}_6\text{-MoS}_2\text{-HCNRs}$  in comparison with  $2\text{H-MoS}_2\text{/HCNRs}$ , disclosing the generation of the N–Mo–S triatomic interface and in-plane electronic coupling between  $\text{MoS}_2$  and  $\text{Mo}_5\text{N}_6$ ; (f) schematic illustration depicts the energy band of the Schottky-type  $\text{Mo}_5\text{N}_6\text{-MoS}_2$  heterojunction, where the electron is transferred from  $2\text{H-MoS}_2$  to  $\text{Mo}_5\text{N}_6$  due to the metallic  $\text{Mo}_5\text{N}_6$ /semiconducting  $\text{MoS}_2$  heterojunction ( $E_{\text{vac}}$  = vacuum energy,  $E_g$  = energy gap,  $E_c$  = conduction band,  $E_f$  = Fermi level,  $E_v$  = valence band,  $\Phi$  = depletion region, and  $W$  = work function) (reproduced with permission from ref. 108 Copyright 2022, Wiley-VCH GmbH).



charge transfer resistance for the HER than  $\text{CuNC}_3$ .  $\text{CuNC}_3$  exhibits higher activity, higher electrochemical surface area, and lower charge transfer resistance for the OER than  $\text{CoN}_{0.73}\text{Co}_3$ .  $\text{CoN}_{0.73}\text{Co}_3$  is antiperovskite  $\text{CoN}_{0.73}\text{Co}_3$  having a cubic crystal structure. It contains Co and N, which are homogeneously distributed. It possesses nanowire-like morphology.  $\text{CuNC}_3$  is antiperovskite  $\text{CuNC}_3$ , having a cubic crystal structure. It contains Co, Cu, and N, which are homogeneously distributed. It possesses nanosheet morphology. For the HER in 1 M KOH, it affords an  $\eta$  of  $-31$  mV at  $-10$  mA  $\text{cm}^{-2}$ , suggesting its very high activity. For overall water splitting in 1 M KOH,  $\text{CuNC}_3^{\text{OER}}/\text{CoN}_{0.73}\text{Co}_3^{\text{HER}}$  affords a potential of 1.53 V at 10 mA  $\text{cm}^{-2}$ , suggesting its very high activity.

Besides, Hu *et al.*<sup>20</sup> observed that  $\text{Co}_2\text{N}_{0.67}/\text{CoMoO}_4$  exhibits enhanced activity and stability for the HER and OER. It was prepared on cleaned carbon cloth by hydrothermal treatment followed by hydrothermal treatment followed by annealing at 400 °C for 5 h under an  $\text{NH}_3$  atmosphere.  $\text{Co}_2\text{N}_{0.67}/\text{CoMoO}_4$  exhibits higher activity and lower charge transfer resistance for the HER and OER than  $\text{Co}_2\text{N}_{0.67}$  and  $\text{CoMoO}_4$ . It exhibits a heterointerface between  $\text{Co}_2\text{N}_{0.67}$  and  $\text{CoMoO}_4$  phases. It contains Mo, Co, O, and N, which are homogeneously distributed. It contains  $\text{Co}^{2+}$ ,  $\text{Mo}^{4+}$ , Co–N and pyridinic N. It possesses nanosheet morphology, where the nanosheet is composed of numerous nanoparticles. For the HER in 1 M KOH, it affords an  $\eta$  of  $-63$  mV at  $-10$  mA  $\text{cm}^{-2}$  and an  $\eta$  of  $-315$  mV at high current density of  $-1000$  mA  $\text{cm}^{-2}$ , suggesting its very high activity. For overall water splitting in 1 M KOH,  $\text{Co}_2\text{N}_{0.67}/\text{CoMoO}_4$  affords a potential of 1.71 V at 100 mA  $\text{cm}^{-2}$  and 1.98 V at a current density of 1000 mA  $\text{cm}^{-2}$ , suggesting its very high activity.

Fabricating the Mott–Schottky heterointerface comprising metallic and semiconductor heterojunctions could tune the interfacial charge polarization and provide an optimal band structure, boosting the intrinsic activity for the HER. Pi *et al.*<sup>108</sup> observed that  $\text{Mo}_5\text{N}_6\text{-MoS}_2\text{-HCNRs}$  (HCNRs: hollow carbon nanoribbons) exhibit outstanding activity and stability for the HER. It was prepared by hydrothermal treatment followed by chemical polymerization followed by hydrothermal treatment (220 °C for 36 h) followed by thermal nitridation (750 °C under an  $\text{NH}_3$  atmosphere).  $\text{Mo}_5\text{N}_6\text{-MoS}_2\text{-HCNRs}$  exhibit higher activity and electrochemical surface area for the HER than  $\text{MoS}_2\text{-HCNRs}$  and  $\text{Mo}_5\text{N}_6\text{-HCNRs}$ . It is composed of  $\text{Mo}_5\text{N}_6\text{-MoS}_2$  nanosheets, which are grown on hollow carbon nanoribbons. It is polycrystalline, which contains  $\text{Mo}_5\text{N}_6$  and 2H- $\text{MoS}_2$  phases with heterointerfaces. It contains Mo, N, S, and C, which are homogeneously distributed. In the high-resolution XPS spectra, the Mo 3d peak of  $\text{Mo}^{4+}$  (Fig. 6a) and S 2p peak of  $\text{S}^{2-}$  (Fig. 6b) of  $\text{Mo}_5\text{N}_6\text{-MoS}_2\text{-HCNRs}$  exhibit slight positive shifts when compared to those of  $\text{MoS}_2\text{-HCNRs}$ , suggesting a modified electronic structure, where partial electrons could be transferred from  $\text{MoS}_2$  to  $\text{Mo}_5\text{N}_6$ . The Mo K-edge XANES spectra (Fig. 6c) disclose that the valence state of Mo in  $\text{Mo}_5\text{N}_6\text{-MoS}_2\text{-$

HCNRs is almost closer to that of Mo foil, while the  $\text{Mo}_5\text{N}_6\text{-MoS}_2\text{-HCNRs}$  exhibit a lower valence state than  $\text{MoS}_2\text{-HCNRs}$  and  $\text{MoO}_3$ . In the FT-EXAFS curves (Fig. 6d), the  $\text{MoS}_2\text{-HCNRs}$  exhibit peaks for Mo–Mo, Mo–S, and Mo–O, whereas the  $\text{Mo}_5\text{N}_6\text{-MoS}_2\text{-HCNRs}$  exhibit peaks for Mo–N (1.5 Å), Mo–Mo, Mo–S, and Mo–O with a slight shift of positions for Mo atoms. In the radial distance  $K$ -space of Mo K-edge EXAFS (Fig. 6e), the WT intensity maximum of  $\text{Mo}_5\text{N}_6\text{-MoS}_2\text{-HCNRs}$  is at 6.0 Å corresponding to the Mo–S bond in pristine  $\text{MoS}_2$ , which is higher than that of the 5.6 Å in 2H- $\text{MoS}_2/\text{HCNRs}$ , suggesting the generation of the N–Mo–S triatomic interface and synergistic electronic coupling. The work functions of 2H- $\text{MoS}_2$  and  $\text{Mo}_5\text{N}_6$  are 5.83 and 7.62 eV, respectively, where the former corresponds to semiconductor characteristics and the latter to metallic characteristics. On integrating 2H- $\text{MoS}_2$  with  $\text{Mo}_5\text{N}_6$  (Fig. 6f), a Mott–Schottky heterojunction comprising metallic  $\text{Mo}_5\text{N}_6$  and semiconductor 2H- $\text{MoS}_2$  can be formed, which can cause the transfer of valence electrons from 2H- $\text{MoS}_2$  to  $\text{Mo}_5\text{N}_6$  till the system reaches equilibrium, and that could boost the HER kinetics. For the HER in 1 M KOH, it affords an  $\eta$  of  $-53$  mV at  $-10$  mA  $\text{cm}^{-2}$  and an  $\eta$  of  $-315$  mV at a current density of  $-1000$  mA  $\text{cm}^{-2}$ , suggesting its outstanding activity. In contrast, it undergoes negligible decay for 33 h, suggesting its very high stability.

Besides, Zhai *et al.*<sup>109</sup> fabricated a heterostructured NiMoN/NiFe LDH array through hydrothermal treatment followed by nitridation followed by electrodeposition, where the amorphous NiFe LDH nanosheets on NiMoN nanorods could modify the electronic structure, enhance the conductivity, improve the charge transport, and facilitate the evolution of gas. For the OER in 1 M KOH, it affords an  $\eta$  of 266 mV at a current density of 1000 mA  $\text{cm}^{-2}$ , suggesting its very high activity, while it affords high stability. The design of a lamella-heterostructured nanoporous self-supported catalyst could expose abundant active sites, facilitate electron transfer, enhance conductivity, and enhance the performance of the OER. Zeng *et al.*<sup>110</sup> demonstrated a self-supported catalytic bimetallic iron–cobalt alloy/oxyhydroxide and cerium oxynitride ( $\text{FeCo/CeO}_{2-x}\text{N}_x$ ) having a nanoporous lamella-heterostructure as the high-performance catalyst for the OER. The catalyst was prepared by alloying/de-alloying lamella-nanostructured eutectic intermetallic compounds, followed by subsequent thermal nitridation. The 3D nanoporous architecture could expose abundant active sites, while the heterostructure could facilitate mass transport and electron transfer. For the OER in 1 M KOH, it affords an  $\eta$  of 360 mV at a current density of  $>3900$  mA  $\text{cm}^{-2}$ , suggesting its very high activity, while it shows robust stability at a current density of  $\sim 1900$  mA  $\text{cm}^{-2}$  for  $>1000$  h.

## 2.5. Constructing carbon-based electrocatalysts

Fabrication of a Ni–C hybrid nanosheet array with dual nanoislands (one is metallic Ni and the other is metallic Ni coated by C) could modify the electronic structure, enhance the conductivity, expose abundant active sites, and that could enhance the



performance for the HER and OER. Zhu *et al.*<sup>111</sup> observed that the Ni-C hybrid nanosheet array exhibits enhanced activity for the HER and OER. The following steps were involved in its synthesis: at first, Ni MOF was prepared on pretreated Ni foam by hydrothermal treatment. Finally, Ni-C was obtained by annealing the Ni MOF at 450 °C for 2 h under an N<sub>2</sub> atmosphere. The Ni-C hybrid nanosheet array exhibits higher activity and lower charge transfer resistance for the HER than the Ni@C

nanosheet array, Ni nanosheet array, and Ni MOF. It is a Ni-C hybrid nanosheet array, where the nanosheet comprises uniformly dispersed nanoparticles. It exhibits dual nanoislands on nanosheets, where one is a metallic Ni particle, and the other is a metallic Ni core with a graphitic C shell. It contains Ni and C, which are homogeneously distributed. For the HER in 1 M KOH, it affords an  $\eta$  of -37 mV at -10 mA cm<sup>-2</sup>, suggesting its very high activity, and it undergoes almost negligible decay at

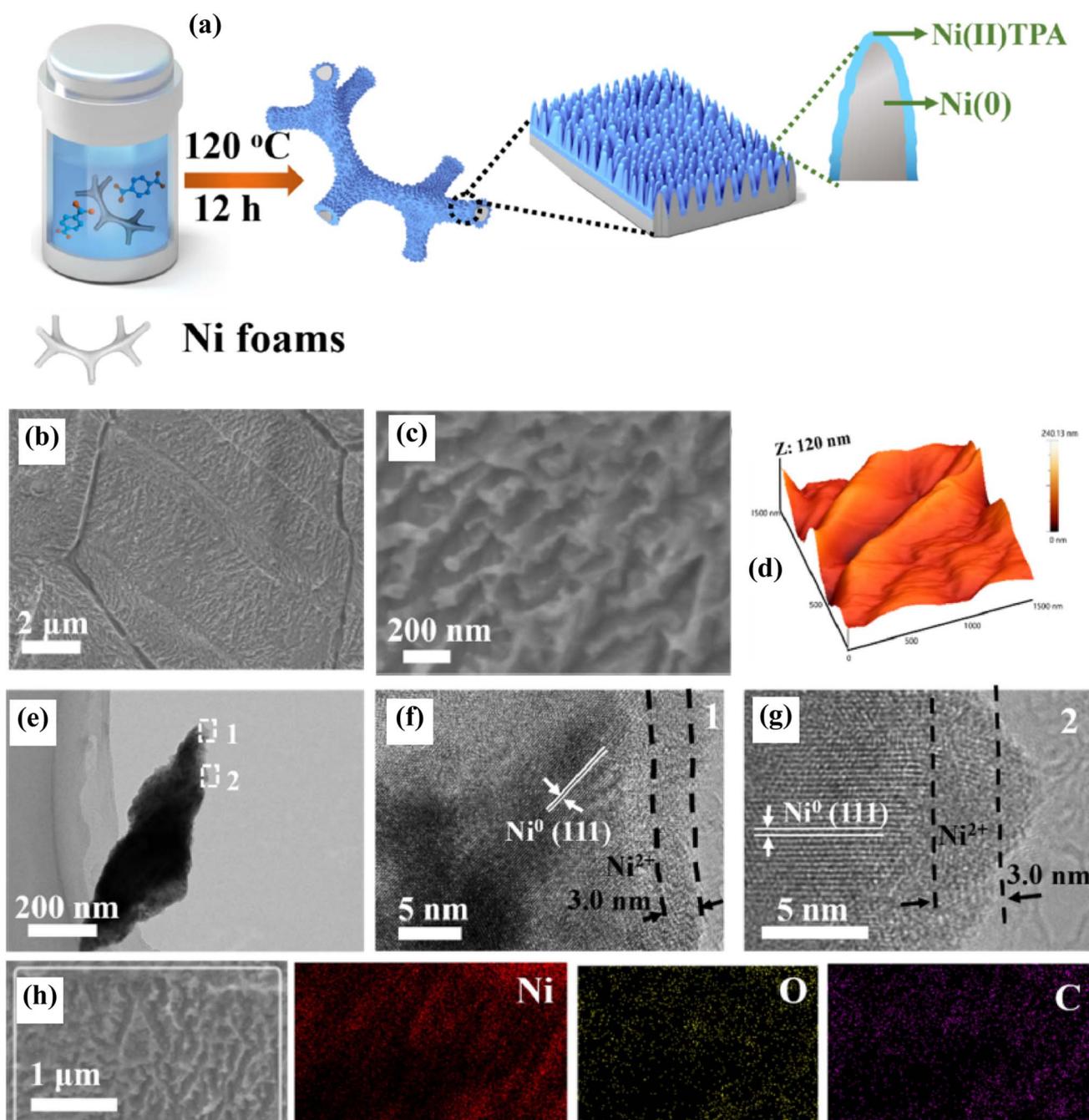


Fig. 7 Synthesis and characterization of KT-Ni(0)@Ni(II)-TPA: (a) schematic diagram depicting the preparation process through a hydrothermal reaction using TPA; (b and c) SEM images; (d) 3D surface architecture obtained using AFM; (e) TEM image; (f) and (g) HRTEM images; (h) SEM image and its corresponding elemental mapping (reproduced with permission from ref. 112 Copyright 2021, Elsevier B.V.).



$-190 \text{ mA cm}^{-2}$  after 10 000 cycles of CV, suggesting its high durability. For overall water splitting in 1 M KOH, Ni-C//Ni-C affords a potential of  $\sim 1.45 \text{ V}$  at  $50 \text{ mA cm}^{-2}$ , suggesting its very high activity.

Constructing a well-controlled core-shell heterostructured electrocatalyst with a superaerophobic surface could provide optimal adsorption energy with intermediates, and facilitate the evolution of gas, and that could enhance the activity and stability of the OER and HER. Hu *et al.*<sup>112</sup> observed that KT-Ni(0)@Ni(II)-TPA exhibits outstanding activity for the OER and it exhibits enhanced activity for the HER, and it was prepared by hydrothermal treatment (Fig. 7a), where a terephthalic acid (TPA)-regulated etching strategy is used on Ni foam for the preparation of a karst topography (KT) featured electrode containing core-shell structured Ni(0)@Ni(II)-TPA. KT-Ni(0)@Ni(II)-TPA exhibits higher activity for the OER than Ni(0)@Ni(II)-TPA and Ni(II)-TPA. It is a karst topography featured electrode containing core-shell structured Ni(0)@Ni(II)-TPA, where the Ni(0) as a core is surrounded by a thin amorphous Ni(II) complex as a shell with the thickness of  $\sim 3.0 \text{ nm}$  (Fig. 7f and g). The karst topography (Fig. 7a-c) is composed of arrays of tall towers and low valleys, where the tall tower is  $\sim 120 \text{ nm}$  in height (Fig. 7d) and  $\sim 700 \text{ nm}$  in length (Fig. 7e). It possesses a superaerophobic surface. It contains Ni, O, and C (Fig. 7h), which are homogeneously distributed. For the OER in 1 M KOH, it affords an  $\eta$  of 197 mV at  $10 \text{ mA cm}^{-2}$  and an  $\eta$  of 380 mV at a current density of  $1500 \text{ mA cm}^{-2}$ , suggesting its outstanding activity, while it affords reasonable stability at an  $\eta$  of 206 mV to 370 mV for  $>45 \text{ h}$ , suggesting its very high stability.

Fabrication of a metallic Co and N dual doped carbon nanosheet array on copper foam could modify the electronic structure, improve the conductivity, expose more active sites, and enhance the performance for the HER. Xin *et al.*<sup>113</sup> observed that CoNC exhibits enhanced activity for the HER. The following steps were involved in its synthesis: at first, ZIF-L was grown on pretreated Cu foam by immersing in an aqueous solution of  $\text{Co}(\text{NO}_3)_2$  and 2-methylimidazole for 1 h at room temperature. The recrystallized ZIF-L was obtained by immersing it in a fresh aqueous solution of Co ion and 2-methylimidazole. Finally, CoNC was obtained by pyrolyzing the recrystallized ZIF-L at  $500 \text{ }^\circ\text{C}$  for 2 h under an Ar atmosphere. The CoNC on Cu foam exhibits higher activity, higher electrochemical surface area, and lower charge transfer resistance for the HER than CoNC on Ni foam. It is a metallic Co and N dual-doped carbon nanosheet array. It contains graphitic N, pyridinic N, pyrrolic N, and Co-N. For the HER in 1 M KOH, it affords an  $\eta$  of  $-64 \text{ mV}$  at  $-10 \text{ mA cm}^{-2}$ , suggesting its very high activity.

ZIF-67 represents a Co-based zeolitic imidazolate framework. The introduction of water in the synthesis of modified-ZIF-67 could alter the morphology and phase of the modified-ZIF-67, generating CoOOH with abundant oxygen vacancies as active species during the OER. In contrast, the heat and acid treatments of modified ZIF-67 could form active species for the HER. Lei *et al.*<sup>114</sup> observed that M-Co-CN exhibits enhanced activity

for the HER, while the activated-modified-ZIF-67 exhibits enhanced activity and stability for the OER. The modified-ZIF-67 was obtained by the precipitation method at  $0 \text{ }^\circ\text{C}$ , where a de-ionized water/methanol/isobutanol mixture solution was used. M-Co-CN was synthesized by heat treatment of modified-ZIF-67 at  $900 \text{ }^\circ\text{C}$  for 2 h under an Ar atmosphere followed by acid treatment. The activated-modified-ZIF-67 was obtained by the electrochemical activation process of modified-ZIF-67. The morphology and crystalline phase of the modified ZIF-67 are changed when compared to that of ZIF-67, which could be due to the introduction of water molecules in the synthesis of modified ZIF-67. The modified ZIF-67 possesses nanorod-like morphology, whereas ZIF-67 possesses particle morphology. Moreover, the crystalline phase of modified ZIF-67 is entirely different from that of ZIF-67. In the high-resolution O 1s XPS spectrum of modified-ZIF-67, the peaks at 532.0 eV and 535.2 eV are ascribed to the  $-\text{OH}$  and adsorbed  $\text{H}_2\text{O}$ , respectively, while the peak corresponding to adsorbed  $\text{H}_2\text{O}$  for modified-ZIF-67 exhibits a slight shift when compared to that of ZIF-67. The modified ZIF-67 contains Co, C, O, and N, which are homogeneously distributed. The formation of CoOOH with abundant oxygen vacancies on modified-ZIF-67 during the OER process is much easier when compared to that of ZIF-67, which could be due to the change in the morphology and crystalline phase of the modified-ZIF-67. M-Co-CN exhibits higher activity for the HER than Co-CN. The activated-modified-ZIF-67 exhibits higher activity and lower charge transfer resistance for the OER than modified-ZIF-67, activated-ZIF-67, and ZIF-67. For the OER in 1 M KOH, the activated-modified-ZIF-67 affords an  $\eta$  of 175 mV at  $10 \text{ mA cm}^{-2}$ , suggesting its very high activity, while it affords 96.6% retention at  $100 \text{ mA cm}^{-2}$  for 100 h, suggesting its very high stability. For the HER in 1 M KOH, M-Co-CN affords an  $\eta$  of  $-80 \text{ mV}$  at  $-10 \text{ mA cm}^{-2}$ , suggesting its very high activity. For overall water splitting in 1 M KOH, the activated-modified-ZIF-67<sup>OER</sup>//M-Co-CN<sup>HER</sup> affords a potential of 1.51 V at  $10 \text{ mA cm}^{-2}$ , suggesting its very high activity, while it affords 93.7% retention at  $20 \text{ mA cm}^{-2}$  for 100 h, suggesting its very high stability.

Fabrication of Co and N dual-doped carbon nanotubes having an abundance of atomically dispersed low-coordinate Co-N sites could provide optimal adsorption energy with intermediates, enhancing HER performance. Ding *et al.*<sup>115</sup> observed that Co-900-A exhibits enhanced activity for the HER. Co-900-A represents acid-treated Co-900, where Co-900 indicates Co and N co-doped carbon nanotubes with an abundance of atomically dispersed low-coordinate Co-N sites. Co-900-A contains Co, C, and N, which are homogeneously distributed. Co-900 was prepared by the precipitation method followed by pyrolysis at  $950 \text{ }^\circ\text{C}$  for 1 h under an  $\text{N}_2$  atmosphere, followed by stirring with reflux for 4 h and heat treatment at  $900 \text{ }^\circ\text{C}$  for 1 h under an  $\text{N}_2$  atmosphere.

Besides, Liu *et al.*<sup>116</sup> observed that Ni-Mo<sub>2</sub>C-0.67 exhibits enhanced activity and stability for the HER. It was prepared on a Ni plate cathode by electrodeposition in molten LiF-NaF-KF-



$\text{Na}_2\text{MoO}_4\text{-K}_2\text{CO}_3$  salts at 750 °C. Ni-Mo<sub>2</sub>C-0.67 is Ni-doped Mo<sub>2</sub>C. It contains Mo<sup>2+</sup>, Mo<sup>3+</sup>, Mo<sup>4+</sup>, and Mo<sup>6+</sup>, where Mo<sup>2+</sup> and Mo<sup>3+</sup> could be ascribed to Mo-C in Mo<sub>2</sub>C, while Mo<sup>4+</sup> and Mo<sup>6+</sup> could be attributed to MoO<sub>2</sub> and MoO<sub>3</sub>, respectively, possibly due to the oxidation in air. It possesses a porous 3D flower-like morphology, which is composed of nanosheets. The contact angle of Ni-Mo<sub>2</sub>C-0.67 is 0°, suggesting its superhydrophilic surface and high wettability, which could enhance the electrolyte interaction and facilitate the gas evolution. The DFT calculations disclose that the  $\Delta G_{\text{H}^*}$  value of optimized Ni-Mo<sub>2</sub>C-0.67 was calculated to be -0.13 eV, suggesting its enhanced intrinsic HER catalytic activity. For the HER in 1 M KOH, it affords an  $\eta$  of -151 mV at -10 mA cm<sup>-2</sup>, suggesting its very high activity, while it affords reasonable stability for 100 h, suggesting its very high stability.

Moreover, Xu *et al.*<sup>117</sup> observed that Fe/Mo<sub>2</sub>C-NC<sup>OER</sup>//Ni/Mo<sub>2</sub>C-NC<sup>HER</sup> exhibits enhanced activity and stability for overall water splitting. Ni/Mo<sub>2</sub>C-NC or Fe/Mo<sub>2</sub>C-NC was prepared on pretreated Ni foam by the impregnation method followed by carbonization (500 °C for 2 h followed by 750 °C for 2 h) under an Ar atmosphere. Ni/Mo<sub>2</sub>C-NC exhibits higher activity, higher electrochemical surface area, and lower charge transfer resistance for the HER than Mo<sub>2</sub>C-NC, Fe/Mo<sub>2</sub>C-NC, and Co/Mo<sub>2</sub>C-NC. In comparison, Fe/Mo<sub>2</sub>C-NC exhibits higher activity for the OER than Mo<sub>2</sub>C-NC, Ni/Mo<sub>2</sub>C-NC, and Co/Mo<sub>2</sub>C-NC. Ni/Mo<sub>2</sub>C-NC comprises an Ni/Mo<sub>2</sub>C heterostructure, which is embedded in N-doped carbon sheets. In the high-resolution XPS spectra, the Mo 3d peak of Ni/Mo<sub>2</sub>C-NC exhibits a slight negative shift when compared to that of Mo<sub>2</sub>C-NC, suggesting a modified electronic structure in the Ni/Mo<sub>2</sub>C-NC possibly due to the partial transfer of electrons from Ni to Mo<sub>2</sub>C, which could be due to the higher electronegativity of Mo, when compared to that of Ni. For overall water splitting in 1 M KOH, Fe/Mo<sub>2</sub>C-NC<sup>OER</sup>//Ni/Mo<sub>2</sub>C-NC<sup>HER</sup> affords a potential of 1.66 V at 100 mA cm<sup>-2</sup>, suggesting its very high activity.

In addition, Yuan *et al.*<sup>118</sup> observed that Co/Mo<sub>2</sub>C@C exhibits enhanced activity and stability for the HER and OER. It was prepared by stirring, followed by heat treatment for 3 h at 850 °C in an H<sub>2</sub>/Ar atmosphere. Co/Mo<sub>2</sub>C@C exhibits higher activity and lower charge transfer resistance for the HER and OER than Mo<sub>2</sub>C@C. It comprises a cubic Co and hexagonal  $\beta$ -Mo<sub>2</sub>C heterostructure supported on carbon. The carbon could be graphitic carbon or disordered carbon. In the high-resolution XPS spectra, the Mo 3d peak of Co/Mo<sub>2</sub>C@C exhibits a slight negative shift when compared to that of Mo<sub>2</sub>C@C, suggesting a modified electronic structure in Co/Mo<sub>2</sub>C@C possibly due to the partial transfer of electrons from Co to Mo<sub>2</sub>C, which could be due to the higher electronegativity of Mo, when compared to that of Co. As a result, the antibonding orbitals of Mo can be filled by the accumulated electrons on Mo<sub>2</sub>C, which could alter the adsorption of H<sub>2</sub>O\* and H\*, enhancing the intrinsic HER catalytic activity. The Mo in Mo<sub>2</sub>C@C is completely oxidized after the OER. On the other hand, the oxidation of Mo in Co/Mo<sub>2</sub>C@C is prevented after the OER, where Co is oxidized into

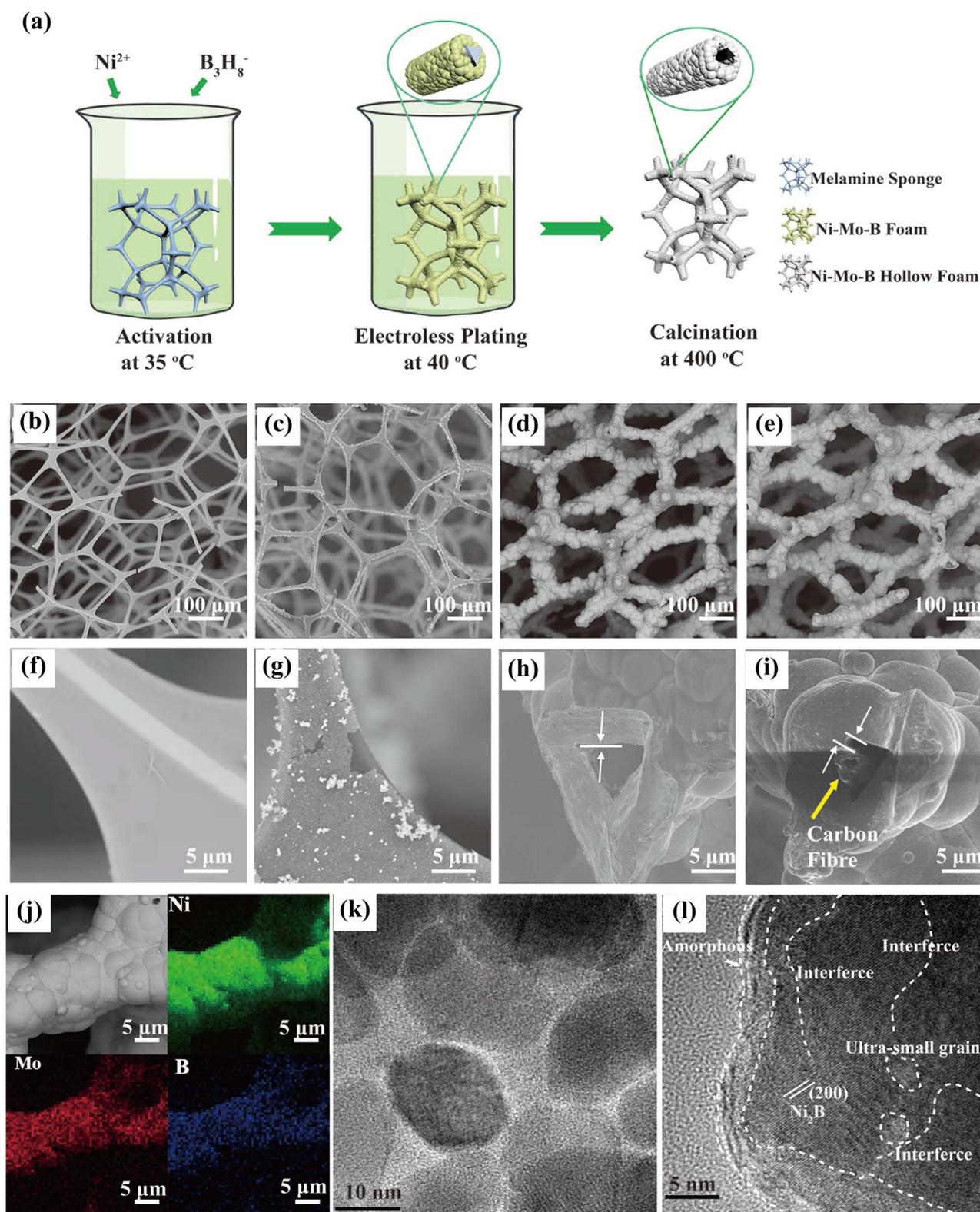
CoOOH, suggesting the self-sacrifice effect of Co. The dissolution and oxidation of Mo<sub>2</sub>C in Co/Mo<sub>2</sub>C@C could be prevented by Co, where the formation of high valence Co ion and the well-preserved Mo<sub>2</sub>C could lead to high stability for the OER. It contains micropores. For the HER in 1 M KOH, it affords an  $\eta$  of -98 mV at -10 mA cm<sup>-2</sup>, suggesting its very high activity.

Besides, Li *et al.*<sup>119</sup> observed that Co-MoC/Mo<sub>2</sub>C exhibits enhanced activity and stability for the HER. It was synthesized by hydrothermal treatment followed by the impregnation method followed by annealing (400 °C for 2 h followed by 750 °C for 2 h) under an Ar atmosphere. Co-MoC/Mo<sub>2</sub>C exhibits higher activity ( $\eta$  at -10 mA cm<sup>-2</sup>), higher electrochemical surface area, and lower charge transfer resistance for the HER than Ni-MoC/Mo<sub>2</sub>C, Fe-MoC/Mo<sub>2</sub>C, Cu-MoC/Mo<sub>2</sub>C, and MoC. It is a Co-MoC/Mo<sub>2</sub>C heterostructure. It exhibits heterogeneous interfaces between  $\alpha$ -MoC and  $\beta$ -Mo<sub>2</sub>C phases. It contains Co, Mo, C, and N, which are homogeneously distributed. It contains Mo<sup>2+</sup>, Mo<sup>3+</sup>, Mo<sup>4+</sup>, and Mo<sup>6+</sup>. In the high-resolution XPS spectra, the Co 2p peak of Co-MoC/Mo<sub>2</sub>C exhibits a slight shift compared to that of Co-Mo<sub>2</sub>C, suggesting a modified electronic structure. It contains pores (about 5.6 nm). It possesses 2D stripe morphology. For the HER in 1 M KOH, it affords an  $\eta$  of -82 mV at -10 mA cm<sup>-2</sup>, suggesting its very high activity.

Moreover, Gong *et al.*<sup>120</sup> observed that Mo<sub>2</sub>C-CoO@NC exhibits enhanced activity and stability for the HER and OER. It was obtained by electrospinning followed by pre-oxidation at 250 °C for 3 h in air and carbonization at 800 °C for 3 h under an N<sub>2</sub> atmosphere. It comprises hexagonal  $\beta$ -Mo<sub>2</sub>C and cubic CoO, which are encapsulated in N-doped carbon nanofiber. It contains pyrrolic-N, pyridinic-N, and graphitic-N. It contains a Mo-N bond, suggesting the existence of interaction between Mo<sub>2</sub>C and N-doped carbon. It contains Mo, Co, N, C, and O, which are homogeneously distributed. For the OER in 1 M KOH, it affords an  $\eta$  of 222 mV at 10 mA cm<sup>-2</sup>, suggesting its very high activity.

In addition, Sun *et al.*<sup>121</sup> observed that Co<sub>2</sub>P/Mo<sub>2</sub>C@NC exhibits enhanced activity and stability for the HER and OER. It was prepared by heating the SiO<sub>2</sub>@CoPMo@dopamine complex for 6 h at 800 °C under an N<sub>2</sub> atmosphere followed by acid treatment (HCl followed by HF). Co<sub>2</sub>P/Mo<sub>2</sub>C@NC exhibits higher activity, higher electrochemical surface area, and lower charge transfer resistance for the HER and OER than Co<sub>2</sub>P@NC and Mo<sub>2</sub>C@NC. It comprises a Co<sub>2</sub>P/Mo<sub>2</sub>C heterojunction, which is supported on N-doped carbon. It contains a Mo-N bond, suggesting the existence of interaction between Mo<sub>2</sub>C and N-doped carbon. It contains Mo<sup>2+</sup>, Mo<sup>4+</sup>, and Mo<sup>6+</sup>. It contains Mo, Co, P, C, and N, which are homogeneously distributed. It possesses a porous structure. The Co<sub>2</sub>P/Mo<sub>2</sub>C@NC//Co<sub>2</sub>P/Mo<sub>2</sub>C@NC electrolyzer using AsGa solar cells exhibits a solar-to-hydrogen conversion efficiency of 18.1%. For the OER in 1 M KOH, it affords an  $\eta$  of 209 mV at 10 mA cm<sup>-2</sup>, suggesting its very high activity. For the HER in 1 M KOH, it affords an  $\eta$  of -86 mV at -10 mA cm<sup>-2</sup>, suggesting its very high activity. For overall water splitting in 1 M KOH, Co<sub>2</sub>P/





**Fig. 8** (a) Schematic diagram depicting the fabrication process of NiMoB hollow foam; (b) and (f) SEM images of bare melamine sponge; (c) and (g) SEM images of activated melamine sponge; (d) and (h) SEM images of Ni-Mo-B foam; (e) and (i) SEM images of NiMoB hollow foam; (j) SEM image and the corresponding EDX elemental mapping of NiMoB hollow foam; (k) and (l) TEM images of NiMoB hollow foam (reproduced with permission from ref. 8 Copyright 2021, Wiley-VCH GmbH).



Mo<sub>2</sub>C@NC//Co<sub>2</sub>P/Mo<sub>2</sub>C@NC affords a potential of 1.55 V at 10 mA cm<sup>-2</sup>, suggesting its very high activity.

Besides, Luo *et al.*<sup>21</sup> observed that MoS<sub>2</sub>/Mo<sub>2</sub>C exhibits enhanced activity and stability for the HER. It was prepared on pretreated Ti foil by hydrothermal treatment followed by chemical vapor deposition at 750 °C with CH<sub>4</sub>. MoS<sub>2</sub>/Mo<sub>2</sub>C exhibits higher activity and lower charge transfer resistance for the HER than MoS<sub>2</sub>. MoS<sub>2</sub>/Mo<sub>2</sub>C is composed of MoS<sub>2</sub> microspheres, and the microspheres comprised MoS<sub>2</sub> nanosheets, where the β-Mo<sub>2</sub>C nanoparticles are decorated on the edges of MoS<sub>2</sub> nanosheets. It contains S, Mo, and C, which are homogeneously distributed. The contact angle of MoS<sub>2</sub>/Mo<sub>2</sub>C is ~0°, suggesting its superhydrophilic surface and high wettability, which could enhance the electrolyte interaction. At the same time, it exhibits a small gas bubble releasing size

(<0.2 mm), which could facilitate the gas evolution. For the HER in 1 M KOH, it affords an η of ~-120 mV at -10 mA cm<sup>-2</sup>, and an η of -220 mV at a current density of -1000 mA cm<sup>-2</sup>, suggesting its very high activity, and it undergoes negligible decay at -10 mA cm<sup>-2</sup> after 10 000 cycles of CV, suggesting its high durability.

## 2.6. Constructing alloy/B/V/F/Si-based electrocatalysts

Fabrication of alloy ribbons by tuning the atomic packing structure could enhance the electron transferring efficiency, reduce the electron binding energy, and enhance the activity for the HER. Liu *et al.*<sup>122</sup> observed that Ni<sub>56.5</sub>Co<sub>35</sub>Ti<sub>8.5</sub> exhibits enhanced activity for the HER. The following steps were involved in the preparation of the Ni<sub>56.5</sub>Co<sub>35</sub>Ti<sub>8.5</sub> alloy ribbon: initially, the master alloy was obtained by arc-melting the

**Table 1** Overpotential (η (Part 1: η from -14 to -127 mV)) to achieve -10 mA cm<sup>-2</sup> for the hydrogen evolution reaction (HER) of various reported noble metal-free electrocatalysts in 1 M KOH alkaline electrolyte (η values to achieve greater than -10 mA cm<sup>-2</sup> are indicated on the η, which is described in the footnote of this table)<sup>a</sup>

Section 1			Section 2		
HER electrocatalysts	η at -10 mA cm <sup>-2</sup> (mV)	Ref.	HER electrocatalysts	η at -10 mA cm <sup>-2</sup> (mV)	Ref.
Mn <sub>1</sub> Ni <sub>1</sub> Co <sub>1</sub> -P	-14	10	Fe@Co/Se <sub>2</sub>	-78	77
FeP/Ni <sub>2</sub> P	-14	18	Fe-CoP	-78	85
NiMoB hollow foam	-18	8	M-Co-CN	-80	114
NiP <sub>2</sub> -FeP <sub>2</sub> @Cu nanoarray	-23.6	13	Co-MoC/Mo <sub>2</sub> C	-82	119
Mn <sub>6</sub> -CoO	-25.6	31	NiCoP	-84	83
CoN <sub>0.73</sub> Co <sub>3</sub>	-31	107	Co <sub>2</sub> P/Mo <sub>2</sub> C@NC	-86	121
Ni <sub>2</sub> P-Ni <sub>12</sub> P <sub>5</sub> @Ni <sub>3</sub> S <sub>2</sub>	-32	72	NiCoFe-P/C	-87	93
Ni/MoO <sub>2</sub> @CN	-33	15	NiS/MoS <sub>2</sub>	-87	64
Ni-C hnsa	-37	111	1T Co-WS <sub>2</sub> /NiTe <sub>2</sub> /Ni	-88	73
Ni <sub>2</sub> P	-37	82	MoSe <sub>2</sub> @NiCo <sub>2</sub> Se <sub>4</sub>	-89	76
NiFeLa LDH/v-MXene	-38	57	C-Ni <sub>1-x</sub> O/3D printed Ni	~-90 <sup>b</sup>	16
S-Co <sub>2</sub> P@Ni <sub>2</sub> P	-43	87	c-NiFe/a-NiFeOOH@NiMo	-91.9 <sup>c</sup>	11
P-CoMoO <sub>4</sub>	-44	40	HR-NiMoO@Ni	-96	38
Fe <sub>2</sub> P-CoP/CeO <sub>2</sub>	-45	101	WCoSe/WCo <sub>3</sub> O <sub>4</sub>	-98	78
MoO <sub>2</sub> /Co	-48	30	Co/Mo <sub>2</sub> C@C	-98	118
Ni <sub>3</sub> S <sub>2</sub> /FeNi <sub>2</sub> S <sub>4</sub>	-50	66	Ni/CeO <sub>2</sub> @N-CNFs	-100	42
W-NiS <sub>2</sub> /MoO <sub>2</sub>	-52	63	hea-d48h	-101	125
Mo <sub>5</sub> N <sub>6</sub> -MoS <sub>2</sub> -HCNRs	-53	108	Ni <sub>3</sub> S <sub>2</sub> -MoS <sub>2</sub>	-103	65
Zn-Fe/Mn@Mn-FeP	-53	28	NiP	-107	88
S-NiFeP-20	-56	91	CoNiP	-107.56	84
VSb/NiPO	-58	105	CoP <sub>3</sub> -Nb <sub>2</sub> P/PCC	-111	95
CoN@NC	-61	106	Ni <sub>3</sub> Fe <sub>0.75</sub> V <sub>0.25</sub> /Ni <sub>3</sub> Fe <sub>0.75</sub> V <sub>0.25</sub> N	-113	129
Co <sub>2</sub> N <sub>0.67</sub> /CoMoO <sub>4</sub>	-63	20	Mo <sub>2</sub> C-CoO@NC	-115	120
CoNC	-64	113	Faceted CuMn <sub>2</sub> O <sub>4</sub>	-116	32
MH-TMO	~-70	1g	Ni-CoP/Co <sub>2</sub> P@NC	-117	97
Ni <sub>2</sub> (1-x)Mo <sub>2x</sub> P	-72	86	MoS <sub>2</sub> /Mo <sub>2</sub> C	~-120	21
Co <sub>0.21</sub> Fe <sub>0.28</sub> (OH)F	-73	130	(Ni-Fe) <sub>x</sub> /NiFe(OH) <sub>y</sub>	-124 <sup>d</sup>	69
MoS <sub>2</sub> -MoO <sub>3-x</sub> /Ni <sub>3</sub> S <sub>2</sub>	-76	67	Fe,Ce-Ni <sub>x</sub> S <sub>y</sub>	-125	61
Fe-Co-CO <sub>3</sub> -OH	-77	17	Bi <sub>2</sub> O <sub>3</sub> based	-127	33

<sup>a</sup> η: overpotential; Ref.: references; PCC: plasma modified carbon cloth; HCNRs: hollow carbon nanoribbons; c-NiFe/a-NiFeOOH@NiMo: crystalline-NiFe/amorphous-NiFeOOH@NiMo; LDH: layered double hydroxide; VSb/NiPO: nickel phosphate microprism, where the microprism is mainly composed of Versailles-Santa Barbara-5, which is a kind of nickel phosphate molecular sieve having the chemical formula of Ni<sub>20</sub>[(OH)<sub>12</sub>(H<sub>2</sub>O)<sub>6</sub>][(HPO<sub>4</sub>)<sub>8</sub>(PO<sub>4</sub>)<sub>4</sub>]·12H<sub>2</sub>O; MH-TMO: mesoporous and heterostructured transition metal oxides; hea-d48h: it is a high-entropy alloy (hea), which is de-alloyed for 48 h, where the Ni<sub>30</sub>Co<sub>30</sub>Cr<sub>10</sub>Fe<sub>10</sub>Al<sub>18</sub>W<sub>2</sub> high-entropy alloy comprises FCC and ordered aluminum-enriched BCC phases, while three dimensional porous architecture is constructed by de-alloying (selective etching of the BCC phase) the high-entropy alloy for 48 h; N-CNFs: N-doped carbon nanofibers; hnsa: hybrid nanosheet array; M-Co-CN: it was synthesized by the heat treatment of modified-ZIF-67 followed by acid treatment, where ZIF-67 represents a Co-based zeolitic imidazolate framework. <sup>b</sup> ~-90 mV at -100 mA cm<sup>-2</sup>. <sup>c</sup> -91.9 mV at -20 mA cm<sup>-2</sup>. <sup>d</sup> -124 mV at -100 mA cm<sup>-2</sup>.



elements (purity: >99.9 wt%). Finally, the alloy ribbon was obtained by re-melting the master alloy in a quartz tube using induction melting, followed by injecting it onto a roller having a spinning tangent speed of about 40 m s<sup>-1</sup>. Ni<sub>56.5</sub>Co<sub>35</sub>Ti<sub>8.5</sub> exhibits higher activity and lower charge transfer resistance for the HER than Ni<sub>57.5</sub>Co<sub>35</sub>Ti<sub>7.5</sub>, Ni<sub>50</sub>Co<sub>37</sub>Ti<sub>13</sub>, and Ni<sub>46</sub>-Co<sub>35.5</sub>Ti<sub>18.5</sub>. The enhanced activity of Ni<sub>56.5</sub>Co<sub>35</sub>Ti<sub>8.5</sub> for the HER is ascribed to low electron binding energy and low atomic packing density.

**Table 2** Overpotential ( $\eta$  (Part 2:  $\eta$  from -128 to -425 mV)) to achieve -10 mA cm<sup>-2</sup> for the hydrogen evolution reaction (HER) of various reported noble metal-free electrocatalysts in an alkaline electrolyte ( $\eta$  to achieve greater than -10 mA cm<sup>-2</sup> are indicated on the  $\eta$ , which is described in the footnote of this table)<sup>a</sup>

HER electrocatalysts	$\eta$ at -10 mA cm <sup>-2</sup> (mV)	Electrolyte	Ref.
Ni <sub>2</sub> P-Fe <sub>2</sub> P	-128	1 M KOH	19
Ni/Mo <sub>2</sub> C-NC	-131 <sup>b</sup>	1 M KOH	117
Ce@NiCo LDH	-134 <sup>c</sup>	1 M KOH	55
NiP <sub>2</sub> /NbP@CNTs	-137 <sup>d</sup>	1 M KOH	96
MoO <sub>3</sub> -Co(OH) <sub>2</sub> @Ag	-142	1 M KOH	39
Ni-Mo <sub>2</sub> C-0.67	-151	1 M KOH	116
Cu <sub>3</sub> P-Cu <sub>2</sub> O/NPC	~ -155	1 M KOH	100
SAE <sub>HER</sub> -ECT-NiSi	-156 <sup>e</sup>	1 M KOH	132
CoP-NC@NiFeP	~ -163 <sup>f</sup>	1 M KOH	98
e-FeCoNiCu-P	-165	1 M KOH	89
Fe-NiS-NiS <sub>2</sub>	-167	1 M KOH	62
c-CoMnP/a-CoMn LDH	-170.3 <sup>g</sup>	1 M KOH	56
Sn-Ni <sub>3</sub> S <sub>2</sub>	-171 <sup>h</sup>	1 M KOH	14
Co <sub>3</sub> O <sub>4</sub>	-177	1 M KOH	29
Ni <sub>x</sub> S <sub>y</sub> @MnO <sub>x</sub> H <sub>y</sub>	-179	1 M KOH	68
Co-Mn-CO <sub>3</sub> -OH	-180	1 M KOH	48
NiFe LDH <sup>activated</sup>	-189	1 M KOH	51
Co-Ni <sub>3</sub> S <sub>2</sub>	-192	1 M NaOH	58
Ni <sub>2</sub> P/NC	-201	1 M KOH	92
Co-Ni <sub>3</sub> S <sub>2</sub>	-220 <sup>i</sup>	1 M KOH	59
KT-Ni(0)@Ni(n)-TPA	-228	1 M KOH	112
Fe <sub>2</sub> P/Co@NPC	-235	1 M KOH	6e
Co-900-A	-246	1 M KOH	115
LSCO-MoSe <sub>2</sub>	-260	1 M KOH	9
Ni-FePS <sub>3</sub>	-356	1 M KOH	71
Fe <sub>62.5</sub> (CoNi) <sub>27.5</sub> Cr <sub>10</sub>	-378	1 M NaOH	123
LSC-N-GQDs-MoSe <sub>2</sub>	-409	1 M KOH	80
Ni <sub>56.5</sub> Co <sub>35</sub> Ti <sub>8.5</sub>	-425 <sup>j</sup>	1 M KOH	122

<sup>a</sup>  $\eta$ : overpotential; LDH: layered double hydroxide; Co-900-A: it represents acid treated Co-900, where Co-900 indicates Co and N co-doped carbon nanotubes with an abundance of low-coordinate Co-N sites; e-FeCoNiCu-P: electrochemically etched FeCoNiCu-P; CNTs: carbon nanotubes; c-CoMnP/a-CoMn LDH: crystalline CoMnP decorated amorphous CoMn LDH; KT-Ni(0)@Ni(n)-TPA: a terephthalic acid (TPA)-regulated etching strategy is used for the preparation of a karst topography (KT) featured electrode containing core-shell structured Ni(0)@Ni(n)-TPA; LSC/LSCO: La<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3- $\delta$</sub> ; N-GQDs: N-doped graphene quantum dots; SAE<sub>HER</sub>-ECT-NiSi: NiSi is subjected to ECT followed by SAE<sub>HER</sub>, where ECT is an electrochemical tuning process comprising lithiation and rapid delithiation of NiSi, while SAE<sub>HER</sub> is a self-adaptive evolution that involves conducting multiple linear sweep voltammetry on ECT-NiSi under HER conditions. <sup>b</sup> -131 mV at -100 mA cm<sup>-2</sup>. <sup>c</sup> -134 mV at -50 mA cm<sup>-2</sup>. <sup>d</sup> -137 mV at -20 mA cm<sup>-2</sup>. <sup>e</sup> -156 mV at -100 mA cm<sup>-2</sup>. <sup>f</sup> -163 mV at -50 mA cm<sup>-2</sup>. <sup>g</sup> -170.3 mV at -100 mA cm<sup>-2</sup>. <sup>h</sup> -171 mV at -100 mA cm<sup>-2</sup>. <sup>i</sup> -220 mV at -50 mA cm<sup>-2</sup>. <sup>j</sup> -425 mV at -500 mA cm<sup>-2</sup>.

Anodization followed by electrochemical activation of the Fe<sub>60</sub>(CoNi)<sub>30</sub>Cr<sub>10</sub> medium entropy alloy could generate an optimal metal (oxy)hydroxide layer as active sites on the surface, enhance the conductivity, increase the surface wettability, expose abundant active sites, and that could enhance the activity for the OER. Park *et al.*<sup>123</sup> observed that Fe<sub>62.5</sub>(CoNi)<sub>27.5</sub>Cr<sub>10</sub> exhibits enhanced activity for the HER, while the activated Fe<sub>60</sub>(CoNi)<sub>30</sub>Cr<sub>10</sub> exhibits enhanced activity for the OER. The activated Fe<sub>60</sub>(CoNi)<sub>30</sub>Cr<sub>10</sub> was prepared by the anodization of Fe<sub>60</sub>(CoNi)<sub>30</sub>Cr<sub>10</sub> followed by CV activation. Fe<sub>62.5</sub>(CoNi)<sub>27.5</sub>Cr<sub>10</sub> exhibits higher activity for the HER than Fe<sub>60</sub>(CoNi)<sub>30</sub>Cr<sub>10</sub>, Fe<sub>57.5</sub>(CoNi)<sub>32.5</sub>Cr<sub>10</sub>, CoCrNi, and CoCr-FeMnNi. Fe<sub>60</sub>(CoNi)<sub>30</sub>Cr<sub>10</sub> exhibits higher activity for the OER than Fe<sub>62.5</sub>(CoNi)<sub>27.5</sub>Cr<sub>10</sub>, Fe<sub>57.5</sub>(CoNi)<sub>32.5</sub>Cr<sub>10</sub>, CoCrNi, and CoCrFeMnNi, while the activated Fe<sub>60</sub>(CoNi)<sub>30</sub>Cr<sub>10</sub> exhibits higher activity and lower charge transfer resistance for the OER than pristine Fe<sub>60</sub>(CoNi)<sub>30</sub>Cr<sub>10</sub> and anodized Fe<sub>60</sub>(CoNi)<sub>30</sub>Cr<sub>10</sub>. Fe<sub>60</sub>(CoNi)<sub>30</sub>Cr<sub>10</sub> is a medium entropy alloy. The contact angle of activated Fe<sub>60</sub>(CoNi)<sub>30</sub>Cr<sub>10</sub> is 35°, suggesting its hydrophilic surface and high wettability, which could enhance the electrolyte interaction. The activated Fe<sub>60</sub>(CoNi)<sub>30</sub>Cr<sub>10</sub> contains an optimal metal (oxy)hydroxide layer as active sites on the surface of Fe<sub>60</sub>(CoNi)<sub>30</sub>Cr<sub>10</sub>. For the OER in 1 M NaOH, the activated Fe<sub>60</sub>(CoNi)<sub>30</sub>Cr<sub>10</sub> affords an  $\eta$  of 187 mV at 10 mA cm<sup>-2</sup>, suggesting its very high activity.

Polymetallic MOF can be obtained by a facile precipitation route at room temperature, while the CoNiCuMnAl high-entropy alloy wrapped in ultra-thin carbon can be prepared by the pyrolysis of the polymetallic MOF followed by acid treatment, and that could generate a metal (oxy)hydroxide as active sites during the OER, enhance the conductivity, and that could enhance the performance for the OER. Wang *et al.*<sup>124</sup> observed that CoNiCuMnAl@C exhibits enhanced activity and stability for the OER. It was obtained by room temperature precipitation followed by pyrolysis at 700 °C for 2 h under an Ar<sub>2</sub>/H<sub>2</sub> atmosphere followed by acid treatment. CoNiCuMnAl@C exhibits higher activity for the OER than CoNiCuMnAl MOF, NiMnCuAl@C, CoMnCuAl@C, CoNiCuMn@C, CuMnAl@C, and CoNiMn@C. It possesses a core-shell structure, where the face-centered cubic CoNiCuMnAl high-entropy alloy as the core is wrapped in ultra-thin carbon as the shell. It exhibits the generation of a metal (oxy)hydroxide as an active species during the OER. For the OER in 1 M KOH, it affords an  $\eta$  of 215 mV at 10 mA cm<sup>-2</sup>, suggesting its very high activity.

The Ni<sub>30</sub>Co<sub>30</sub>Cr<sub>10</sub>Fe<sub>10</sub>Al<sub>18</sub>W<sub>2</sub> high-entropy alloy possesses a unique eutectic dual-phase microstructure comprising face-centered cubic (FCC) and ordered aluminum-enriched body-centered cubic (BCC) phases. Selective etching of the aluminum-enriched BCC phase of Ni<sub>30</sub>Co<sub>30</sub>Cr<sub>10</sub>Fe<sub>10</sub>Al<sub>18</sub>W<sub>2</sub> could construct a three-dimensional porous architecture and increase the oxidation state of the alloying elements, which could expose abundant active sites and enhance the performance of the HER and OER. Han *et al.*<sup>125</sup> observed that hea-d48h exhibits enhanced activity and stability for the HER and OER. hea-d48h is a high-entropy alloy (HEA), which is dealloyed for 48 h, where the Ni<sub>30</sub>Co<sub>30</sub>Cr<sub>10</sub>Fe<sub>10</sub>Al<sub>18</sub>W<sub>2</sub> high-



entropy alloy comprises FCC and ordered aluminum-enriched BCC phases. In comparison, three-dimensional porous architecture is constructed by de-alloying (selective etching of the BCC phase) the high-entropy alloy for 48 h. The following steps were involved in the preparation of the Ni<sub>30</sub>Co<sub>30</sub>Cr<sub>10</sub>Fe<sub>10</sub>Al<sub>18</sub>W<sub>2</sub> high-entropy alloy: at first, the master alloy ingot was obtained by vacuum arc melting. Finally, the high-entropy alloy was obtained by re-melting the ingot four times followed by drop-casting into a copper mold. The high-entropy alloy Ni<sub>30</sub>Co<sub>30</sub>Cr<sub>10</sub>Fe<sub>10</sub>Al<sub>18</sub>W<sub>2</sub> de-alloyed for 48 h (hea-d48h) exhibits higher activity for the HER than bare Ni<sub>30</sub>Co<sub>30</sub>Cr<sub>10</sub>Fe<sub>10</sub>Al<sub>18</sub>W<sub>2</sub>, Ni<sub>30</sub>Co<sub>30</sub>Cr<sub>10</sub>Fe<sub>10</sub>Al<sub>18</sub>W<sub>2</sub> de-alloyed for 12 h, Ni<sub>30</sub>Co<sub>30</sub>Cr<sub>10</sub>Fe<sub>10</sub>Al<sub>18</sub>W<sub>2</sub> de-alloyed for 24 h, and Ni<sub>30</sub>Co<sub>30</sub>Cr<sub>10</sub>Fe<sub>10</sub>Al<sub>18</sub>W<sub>2</sub> de-alloyed for 72 h. High-resolution XPS spectra disclose that both the bare Ni<sub>30</sub>Co<sub>30</sub>Cr<sub>10</sub>Fe<sub>10</sub>Al<sub>18</sub>W<sub>2</sub> alloy and Ni<sub>30</sub>Co<sub>30</sub>Cr<sub>10</sub>Fe<sub>10</sub>Al<sub>18</sub>W<sub>2</sub> de-alloyed for 48 h contain Cr, Fe, Al, Ni, Co, and W, suggesting the existence of all the elements after acid etching. However, the peaks corresponding to Cr, Fe, Al, Ni, Co, and W of Ni<sub>30</sub>Co<sub>30</sub>Cr<sub>10</sub>Fe<sub>10</sub>Al<sub>18</sub>W<sub>2</sub> de-alloyed for 48 h exhibit a positive shift, when compared to that of bare Ni<sub>30</sub>Co<sub>30</sub>Cr<sub>10</sub>Fe<sub>10</sub>Al<sub>18</sub>W<sub>2</sub> alloy, suggesting the

de-alloyed for 72 h. The high-entropy alloy Ni<sub>30</sub>Co<sub>30</sub>Cr<sub>10</sub>Fe<sub>10</sub>Al<sub>18</sub>W<sub>2</sub> de-alloyed for 48 h (hea-d48h) exhibits higher activity and electrochemical surface area for the OER than bare Ni<sub>30</sub>Co<sub>30</sub>Cr<sub>10</sub>Fe<sub>10</sub>Al<sub>18</sub>W<sub>2</sub>, Ni<sub>30</sub>Co<sub>30</sub>Cr<sub>10</sub>Fe<sub>10</sub>Al<sub>18</sub>W<sub>2</sub> de-alloyed for 12 h, Ni<sub>30</sub>Co<sub>30</sub>Cr<sub>10</sub>Fe<sub>10</sub>Al<sub>18</sub>W<sub>2</sub> de-alloyed for 24 h, and Ni<sub>30</sub>Co<sub>30</sub>Cr<sub>10</sub>Fe<sub>10</sub>Al<sub>18</sub>W<sub>2</sub> de-alloyed for 72 h. High-resolution XPS spectra disclose that both the bare Ni<sub>30</sub>Co<sub>30</sub>Cr<sub>10</sub>Fe<sub>10</sub>Al<sub>18</sub>W<sub>2</sub> alloy and Ni<sub>30</sub>Co<sub>30</sub>Cr<sub>10</sub>Fe<sub>10</sub>Al<sub>18</sub>W<sub>2</sub> de-alloyed for 48 h contain Cr, Fe, Al, Ni, Co, and W, suggesting the existence of all the elements after acid etching. However, the peaks corresponding to Cr, Fe, Al, Ni, Co, and W of Ni<sub>30</sub>Co<sub>30</sub>Cr<sub>10</sub>Fe<sub>10</sub>Al<sub>18</sub>W<sub>2</sub> de-alloyed for 48 h exhibit a positive shift, when compared to that of bare Ni<sub>30</sub>Co<sub>30</sub>Cr<sub>10</sub>Fe<sub>10</sub>Al<sub>18</sub>W<sub>2</sub> alloy, suggesting the

**Table 3** Long-term stability (Part 1: 30 h to 400 h of duration) of various reported noble metal-free electrocatalysts for the hydrogen evolution reaction (HER) in 1 M KOH alkaline electrolyte<sup>a</sup>

HER electrocatalysts	Chr amp	Chr pot	Dur (h)	Remark after the stability test	Ref.
NiFeLa LDH/v-MXene	NA	Yes	400	Reasonable stability at a CD of $-100 \text{ mA cm}^{-2}$	57
Ni/MoO <sub>2</sub> @CN	NA	Yes	200	Negligible decay at a CD of $-1000 \text{ mA cm}^{-2}$	15
Ni <sub>2(1-x)</sub> Mo <sub>2x</sub> P	Yes	NA	160	Reasonable stability	86
P-CoMoO <sub>4</sub>	NA	Yes	100	Negligible decay at a CD of $-50 \text{ mA cm}^{-2}$	40
MH-TMO	NA	Yes	100	Reasonable stability at a CD of $-10 \text{ mA cm}^{-2}$	1g
HR-NiMoO@Ni	NA	Yes	100	Reasonable stability at a CD of $-1000 \text{ A m}^{-2}$	38
Ni-Mo <sub>2</sub> C-0.67	Yes	NA	100	Reasonable stability	116
Ni <sub>x</sub> S <sub>y</sub> @MnO <sub>x</sub> H <sub>y</sub>	NA	Yes	100	Reasonable stability at a CD of $-100 \text{ mA cm}^{-2}$	68
Cu <sub>3</sub> P-Cu <sub>2</sub> O/NPC	Yes	NA	90	96% retention	100
Zn-Fe/Mn@Mn-FeP	NA	Yes	80	Negligible decay at a CD of $-10 \text{ mA cm}^{-2}$	28
Mn <sub>6</sub> -CoO	Yes	NA	60	83.6% retention	31
Co <sub>2</sub> N <sub>0.67</sub> /CoMoO <sub>4</sub>	NA	Yes	60	Reasonable stability at a CD of $-100 \text{ mA cm}^{-2}$	20
Sn-Ni <sub>3</sub> S <sub>2</sub>	Yes	NA	60	Negligible decay at an $\eta$ of $-223 \text{ mV}$	14
NiP <sub>2</sub> -FeP <sub>2</sub> @Cu nanoarray	NA	Yes	50	Reasonable stability at a CD of $-1000 \text{ mA cm}^{-2}$	13
Ni-C hnsa	Yes	NA	50	Negligible decay at an $\eta$ of $-59 \text{ mV}$	111
CoP <sub>3</sub> -Nb <sub>2</sub> P/PCC	Yes	NA	50	93.6% retention	95
Faceted CuMn <sub>2</sub> O <sub>4</sub>	Yes	NA	50	Negligible decay	32
Ni-CoP/Co <sub>2</sub> P@NC	Yes	NA	50	Negligible decay	97
CoP-NC@NiFeP	NA	Yes	50	Reasonable stability at a CD of $-50 \text{ mA cm}^{-2}$	98
Mn <sub>1</sub> Ni <sub>1</sub> Co <sub>1</sub> -P	Yes	NA	48	92% retention	10
CoN <sub>0.73</sub> Co <sub>3</sub>	Yes	NA	48	81% retention	107
Co/Mo <sub>2</sub> C@C	Yes	NA	48	90.1% retention at an $\eta$ of $-98 \text{ mV}$	118
(Ni-Fe) <sub>S<sub>x</sub></sub> /NiFe(OH) <sub>y</sub>	NA	Yes	48	Negligible decay at a CD of $-120 \text{ mA cm}^{-2}$	69
Ni <sub>2</sub> P-Fe <sub>2</sub> P	NA	Yes	48	Reasonable stability at a CD of $-100/-500 \text{ mA cm}^{-2}$	19
WCoSe/WCo <sub>3</sub> O <sub>4</sub>	NA	Yes	>45	Reasonable stability at a CD of $-100 \text{ mA cm}^{-2}$	78
Fe,Ce-Ni <sub>x</sub> S <sub>y</sub>	NA	Yes	40	Negligible decay at a CD of $-10 \text{ mA cm}^{-2}$	61
SAE <sub>HER</sub> -ECT-NiSi	Yes	NA	35	Negligible decay at an $\eta$ of $-250 \text{ mV}$	132
NiCoFe-P/C	Yes	NA	34	Negligible decay	93
Mo <sub>5</sub> N <sub>6</sub> -MoS <sub>2</sub> -HCNRs	Yes	NA	33	Negligible decay	108
NiP <sub>2</sub> /NbP@CNTs	Yes	NA	33	~88.6% retention at an $\eta$ of $-247 \text{ mV}$	96
Fe <sub>2</sub> P-CoP/CeO <sub>2</sub>	Yes	NA	30	Negligible decay	101
VSb/NiPO	NA	Yes	>30	94.1% retention at a CD of $-100 \text{ mA cm}^{-2}$	105
Fe-CoP	NA	Yes	30	Negligible decay at a CD of $-10 \text{ mA cm}^{-2}$	85
Co <sub>2</sub> P/Mo <sub>2</sub> C@NC	Yes	NA	30	Negligible decay	121
Ni <sub>3</sub> Fe <sub>0.75</sub> V <sub>0.25</sub> /Ni <sub>3</sub> Fe <sub>0.75</sub> V <sub>0.25</sub> N	Yes	NA	30	Reasonable stability	129
Co-Ni <sub>3</sub> S <sub>2</sub>	Yes	NA	30	Negligible decay at an $\eta$ of $-462 \text{ mV}$	59

<sup>a</sup>  $\eta$ : overpotential; Ref.: references; Dur: duration of the stability test; Chr pot: chronopotentiometry; Chr amp: chronoamperometry; NA: not applicable; CD: current density; PCC: plasma modified carbon cloth; HCNRs: hollow carbon nanoribbons; CNTs: carbon nanotubes; LDH: layered double hydroxide; VSb/NiPO: nickel phosphate microprism, where the microprism is mainly composed of Versailles-Santa Barbara-5, which is a kind of nickel phosphate molecular sieve having the chemical formula of Ni<sub>20</sub>[(OH)<sub>12</sub>(H<sub>2</sub>O)<sub>6</sub>][(HPO<sub>4</sub>)<sub>8</sub>(PO<sub>4</sub>)<sub>4</sub>].12H<sub>2</sub>O; MH-TMO: mesoporous and heterostructured transition metal oxides; SAE<sub>HER</sub>-ECT-NiSi: NiSi is subjected to ECT followed by SAE<sub>HER</sub>, where ECT is an electrochemical tuning process comprising lithiation and rapid delithiation of NiSi, while SAE<sub>HER</sub> is a self-adaptive evolution that involves conducting multiple linear sweep voltammetry on ECT-NiSi under HER conditions; hnsa: hybrid nanosheet array.



formation of high valence ions after acid etching. The dealloying of Ni<sub>30</sub>Co<sub>30</sub>Cr<sub>10</sub>Fe<sub>10</sub>Al<sub>18</sub>W<sub>2</sub> for 48 h causes a hierarchically porous structure, which could expose abundant active sites. For overall water splitting in 1 M KOH, hea-d48h//hea-d48h affords a potential of 1.615 V at 10 mA cm<sup>-2</sup>, suggesting its very high activity, while it affords 99.13% retention for 100 h, suggesting its very high stability.

BO<sub>3</sub><sup>3-</sup> incorporated NiFe LDH could be fabricated by a facile electrodeposition method, while the incorporation of BO<sub>3</sub><sup>3-</sup> in NiFe LDH could tune the electronic structure of the Fe atoms by filling into the oxygen vacancies, increase the oxidation state and coordination number of Fe atoms, enhance the conductivity, and that could enhance the performance for the OER. Liao *et al.*<sup>126</sup> observed that the NiFeB exhibits enhanced activity and stability for the OER. It was prepared on pretreated Ni foam by a one-step electrodeposition process by applying potentials for 10 cycles of CV. NiFeB exhibits higher activity, higher electrochemical surface area,

and lower charge transfer resistance for the OER than NiFe LDH. NiFeB is composed of crystalline NiFe LDH, which BO<sub>3</sub><sup>3-</sup> decorates. It contains B, Fe, Ni, and O, which are homogeneously distributed. In the high-resolution XPS spectra, the Fe 2p peak of NiFeB exhibits a slight positive shift when compared to that of NiFe LDH, suggesting a modified electronic structure in NiFeB, possibly due to the partial transfer of electrons from Fe to BO<sub>3</sub><sup>3-</sup>. It exhibits a lesser amount of oxygen vacancies when compared to NiFe LDH. These results suggest that the incorporation of BO<sub>3</sub><sup>3-</sup> in NiFe LDH could tune the electronic structure of the Fe atoms by filling into the oxygen vacancies. Moreover, incorporating BO<sub>3</sub><sup>3-</sup> in NiFe LDH increases the coordination numbers of Fe atoms. It possesses ultrathin nanosheet morphology. For the OER in 1 M KOH, it affords an  $\eta$  of 201 mV at 10 mA cm<sup>-2</sup>, suggesting its very high activity. In contrast, it affords reasonable stability at 500 mA cm<sup>-2</sup> for 100 h, suggesting its high stability.

**Table 4** Long-term stability (Part 2: 10 h to 29 h of duration) of various reported noble metal-free electrocatalysts for the hydrogen evolution reaction (HER) in 1 M KOH alkaline electrolyte, where the electrolyte other than 1 M KOH is indicated on the electrocatalyst<sup>a</sup>

HER electrocatalysts	Chr amp	Chr pot	Dur (h)	Remark after the stability test	Ref.
MoO <sub>3</sub> -Co(OH) <sub>2</sub> @Ag	NA	Yes	29	Reasonable stability at a CD of -100 mA cm <sup>-2</sup>	39
Ni/CeO <sub>2</sub> @N-CNFs	Yes	NA	27	Negligible decay at an $\eta$ of -135 mV	42
CoN@NC	NA	Yes	25	Reasonable stability at a CD of -10 mA cm <sup>-2</sup>	106
NiS/MoS <sub>2</sub>	Yes	NA	25	Reasonable stability	64
FeP/Ni <sub>2</sub> P	NA	Yes	24	Negligible decay at a CD of -100 mA cm <sup>-2</sup>	18
Ni <sub>2</sub> P-Ni <sub>12</sub> P <sub>5</sub> @Ni <sub>3</sub> S <sub>2</sub>	Yes	NA	24	Negligible decay	72
Ni <sub>2</sub> P	Yes	NA	24	Reasonable stability at an $\eta$ of -240 mV to -650 mV	82
MoO <sub>2</sub> /Co	Yes	NA	24	Negligible decay	30
S-NiFeP-20	Yes	NA	24	Reasonable stability	91
1T Co-WS <sub>2</sub> /NiTe <sub>2</sub> /Ni	NA	Yes	24	97% retention at a CD of -50 mA cm <sup>-2</sup>	73
MoSe <sub>2</sub> @NiCo <sub>2</sub> Se <sub>4</sub>	Yes	NA	24	Negligible decay at an $\eta$ of -135 mV	76
Ni <sub>3</sub> S <sub>2</sub> -MoS <sub>2</sub>	NA	Yes	24	Reasonable stability at a CD of -10 mA cm <sup>-2</sup>	65
MoS <sub>2</sub> /Mo <sub>2</sub> C	Yes	NA	24	Negligible decay	21
Ni/Mo <sub>2</sub> C-NC	Yes	NA	24	Reasonable stability	117
Ce@NiCo LDH	Yes	NA	24	Reasonable stability	55
S-Co <sub>2</sub> P@Ni <sub>2</sub> P	Yes	NA	20	Negligible decay	87
Co <sub>0.21</sub> Fe <sub>0.28</sub> (OH)F	NA	Yes	20	Negligible decay at a CD of -20 mA cm <sup>-2</sup>	130
Fe@Co/Se <sub>2</sub>	NA	Yes	20	Negligible decay at a CD of -10 mA cm <sup>-2</sup>	77
Co-MoC/Mo <sub>2</sub> C	Yes	NA	20	Reasonable stability	119
Bi <sub>2</sub> O <sub>3</sub> based	Yes	NA	20	85.4% retention	33
Co-Ni <sub>3</sub> S <sub>2</sub> <sup>1 M NaOH</sup>	NA	Yes	18	Negligible decay	58
Fe <sub>2</sub> P/Co@NPC	NA	Yes	>16	Negligible decay at a CD of -10 mA cm <sup>-2</sup>	6e
Co <sub>3</sub> O <sub>4</sub>	NA	Yes	>15	Negligible decay at a CD of -100 mA cm <sup>-2</sup>	29
NiCoP	Yes	NA	12	87% retention at an $\eta$ of -84 mV	83
Fe-NiS-NiS <sub>2</sub>	Yes	NA	12	Reasonable stability	62
Ni <sub>2</sub> P/NC	Yes	NA	12	92% retention	92
MoS <sub>2</sub> -MoO <sub>3-x</sub> /Ni <sub>3</sub> S <sub>2</sub>	NA	Yes	11	Reasonable stability at a CD of -100 mA cm <sup>-2</sup>	67
Co-Mn-CO <sub>3</sub> -OH	NA	Yes	10	Negligible decay at a CD of -10 mA cm <sup>-2</sup>	48

<sup>a</sup>  $\eta$ : overpotential; Ref.: references; Dur: duration of the stability test; Chr pot: chronopotentiometry; Chr amp: chronoamperometry; NA: not applicable; CD: current density; LDH: layered double hydroxide; N-CNFs: N-doped carbon nanofibers.



Fabrication of transition metal boride electrocatalysts with a 3D hollow structure could modify the electronic structure, provide optimal adsorption energy with intermediates, improve the conductivity, expose abundant active sites, provide high mechanical strength, and facilitate the gas evolution, which could enhance the activity and stability of the HER and OER. Liu *et al.*<sup>8</sup> observed that the NiMoB hollow foam exhibits outstanding activity and stability for the HER and OER. It was synthesized by the following steps (Fig. 8a). At first, the bare melamine sponge was activated at 35 °C for 10 minutes, where the bare 3D melamine sponge possessed a smooth surface (Fig. 8b and f), which was deposited by nanoparticles after activation (Fig. 8c and g). Then, NiMoB was formed by electroless plating at 40 °C for 4 h (Fig. 8d and h). Finally, NiMoB hollow foam was obtained by calcination at 400 °C for 4 h in an N<sub>2</sub> atmosphere (Fig. 8e and i), where the hollow space is observed between the inner wall of NiMoB and carbon fiber (Fig. 8i). The NiMoB hollow foam exhibits higher activity and electrochemical surface area for the HER and OER than NiMoB on the melamine sponge. It contains Ni, Mo, and B

(Fig. 8j), which are homogeneously distributed. The atomic ratio of Ni : Mo : B of the NiMoB hollow foam is 1 : 0.03 : 0.23. It possesses an amorphous and crystalline state (Fig. 8k and l), where the inner part is mainly composed of a crystalline phase, and the outer layer is an amorphous state (thickness:  $\approx 3$  nm). It contains Ni<sub>2</sub>B, Ni<sub>3</sub>B, Ni, MoB<sub>2</sub>, and Mo phases. It exhibits a density of 0.2 g cm<sup>-3</sup>, which is almost nearer to that of nickel foam. It can withstand a pressure of 2.37 MPa during mechanical compression tests, suggesting its high mechanical stability. It exhibits a sheet resistance of 3.56  $\Omega$  sq<sup>-1</sup>, which is less than that of the nickel foam (4.53  $\Omega$  sq<sup>-1</sup>), suggesting its high electrical conductivity. It exhibits low gas mass transfer resistance. For the OER in 1 M KOH, it affords an  $\eta$  of 230 mV at 10 mA cm<sup>-2</sup>, and an  $\eta$  of  $\sim 460$  mV at a current density of 1000 mA cm<sup>-2</sup>, suggesting its outstanding activity, while it undergoes negligible decay at 600 mA cm<sup>-2</sup> after 500 cycles of CV, suggesting its very high durability. For the HER in 1 M KOH, it affords an  $\eta$  of  $-18$  mV at  $-10$  mA cm<sup>-2</sup>, and an  $\eta$  of  $\sim -420$  mV at a huge current density of  $-1000$  mA cm<sup>-2</sup>, suggesting its outstanding activity, while it undergoes

Table 5 Durability of various reported noble metal-free electrocatalysts for the hydrogen evolution reaction (HER) in 1 M KOH alkaline electrolyte<sup>a</sup>

HER electrocatalysts	Cycles of CV	Remark after the durability test	Ref.
Cu <sub>3</sub> P-Cu <sub>2</sub> O/NPC	20 000	Negligible decay at $-45$ mA cm <sup>-2</sup>	100
Sn-Ni <sub>3</sub> S <sub>2</sub>	10 000	Negligible decay at $-1000$ mA cm <sup>-2</sup>	14
Ni-C hnsa	10 000	Almost negligible decay at $-190$ mA cm <sup>-2</sup>	111
MoS <sub>2</sub> /Mo <sub>2</sub> C	10 000	Negligible decay at $-10$ mA cm <sup>-2</sup>	21
NiCoP	10 000	Slight decay at $-140$ mA cm <sup>-2</sup>	83
Fe-Co-CO <sub>3</sub> -OH	10 000	Negligible decay at $-1000$ mA cm <sup>-2</sup>	17
Ni <sub>2(1-x)</sub> Mo <sub>2x</sub> P	5000	Negligible decay at $-700$ mA cm <sup>-2</sup>	86
CoP <sub>3</sub> -Nb <sub>2</sub> P/PCC	5000	Almost negligible decay at $-500$ mA cm <sup>-2</sup>	95
Mn <sub>1</sub> Ni <sub>1</sub> Co <sub>1</sub> -P	5000	Negligible decay at $-10$ mA cm <sup>-2</sup>	10
FeP/Ni <sub>2</sub> P	5000	Negligible decay at $-1000$ mA cm <sup>-2</sup>	18
Ni <sub>2</sub> P	5000	Negligible decay at $-1200$ mA cm <sup>-2</sup>	82
Mn <sub>6</sub> -CoO	3000	9 mV decay	31
Co <sub>2</sub> N <sub>0.67</sub> /CoMoO <sub>4</sub>	3000	Slight decay at $-200$ mA cm <sup>-2</sup>	20
Ni <sub>2</sub> P-Fe <sub>2</sub> P	3000	Negligible decay at $-1000$ mA cm <sup>-2</sup>	19
Co <sub>2</sub> P/Mo <sub>2</sub> C@NC	3000	Negligible decay at $-90$ mA cm <sup>-2</sup>	121
Ni/CeO <sub>2</sub> @N-CNFs	3000	Negligible decay at $-125$ mA cm <sup>-2</sup>	42
MoO <sub>2</sub> /Co	3000	Very slight decay at $-225$ mA cm <sup>-2</sup>	30
NiFeLa LDH/v-MXene	2000	Negligible decay at $-700$ mA cm <sup>-2</sup>	57
Mo <sub>5</sub> N <sub>6</sub> -MoS <sub>2</sub> -HCNRs	2000	Almost negligible decay at $-100$ mA cm <sup>-2</sup>	108
NiS/MoS <sub>2</sub>	2000	Negligible decay at $-175$ mA cm <sup>-2</sup>	64
Fe@Co/Se <sub>2</sub>	2000	Negligible decay at $-10$ mA cm <sup>-2</sup>	77
Ni <sub>3</sub> S <sub>2</sub> /FeNi <sub>2</sub> S <sub>4</sub>	2000	Negligible decay at $-300$ mA cm <sup>-2</sup>	66
Mo <sub>2</sub> C-CoO@NC	2000	Very slight decay at $-200$ mA cm <sup>-2</sup>	120
P-CoMoO <sub>4</sub>	1000	Negligible decay	40
Zn-Fe/Mn@Mn-FeP	1000	Negligible decay at $-200$ mA cm <sup>-2</sup>	28
Co/Mo <sub>2</sub> C@C	1000	Negligible decay at $-50$ mA cm <sup>-2</sup>	118
Fe,Ce-Ni <sub>x</sub> S <sub>y</sub>	1000	Negligible decay at $-225$ mA cm <sup>-2</sup>	61
Co-Ni <sub>3</sub> S <sub>2</sub>	1000	Negligible decay at $-1000$ mA cm <sup>-2</sup>	59
S-NiFeP-20	1000	Negligible decay	91
S-Co <sub>2</sub> P@Ni <sub>2</sub> P	1000	Negligible decay at $-700$ mA cm <sup>-2</sup>	87
Hea-d48h	1000	Negligible decay at $-10$ mA cm <sup>-2</sup>	125
NiMoB hollow foam	500	Negligible decay at $-1000$ mA cm <sup>-2</sup>	8

<sup>a</sup> PCC: plasma modified carbon cloth; N-CNFs: N-doped carbon nanofibers; hnsa: hybrid nanosheet array; HCNRs: hollow carbon nanoribbons; hea-d48h: it is a high-entropy alloy (hea), which is de-alloyed for 48 h, where the Ni<sub>30</sub>Co<sub>30</sub>Cr<sub>10</sub>Fe<sub>10</sub>Al<sub>18</sub>W<sub>2</sub> high-entropy alloy comprises FCC and ordered aluminum-enriched BCC phases, while three dimensional porous architecture is constructed by de-alloying (selective etching of the BCC phase) the high-entropy alloy for 48 h.



negligible decay at  $-1000 \text{ mA cm}^{-2}$  after 500 cycles of CV, suggesting its very high durability. For overall water splitting in 1 M KOH, the NiMoB hollow foam//NiMoB hollow foam affords a potential of 1.431 V at  $10 \text{ mA cm}^{-2}$ , suggesting its very high activity, while it affords reasonable stability at  $5000 \text{ mA cm}^{-2}$  for 20 h, suggesting its very high stability.

Fabrication of nanostructured NiFeV hydroxide on the  $\text{V}_3\text{O}_7$  nanofiber could modify the electronic structure, increase the

oxidation state of Fe, enhance the conductivity, and expose more active sites, which could enhance the performance of the OER. Zhang *et al.*<sup>127</sup> observed that the NiFeV nanofibers exhibit enhanced activity and stability for the OER. It was synthesized by a two-step hydrothermal treatment. The NiFeV nanofibers exhibit higher activity, higher electrochemical surface area, and lower charge transfer resistance for the OER than NiFeV and NiFe. The NiFeV nanofibers are composed of NiFeV

**Table 6** Overpotential ( $\eta$  (Part 1:  $\eta$  from 39 to 270 mV)) to achieve  $10 \text{ mA cm}^{-2}$  for the oxygen evolution reaction (OER) of various reported noble metal-free electrocatalysts in 1 M KOH alkaline electrolyte, where the electrolyte other than 1 M KOH is indicated on the electrocatalyst. ( $\eta$  values to achieve greater than  $10 \text{ mA cm}^{-2}$  are indicated on the  $\eta$ , which are described in the footnote of this table)<sup>a</sup>

Section 1			Section 2		
OER electrocatalysts	$\eta$ at $10 \text{ mA cm}^{-2}$ (mV)	Ref.	OER electrocatalysts	$\eta$ at $10 \text{ mA cm}^{-2}$ (mV)	Ref.
LSCO-MoSe <sub>2</sub>	39	9	Fe,Ce-Ni <sub>x</sub> S <sub>y</sub>	227 <sup>f</sup>	61
c-NiFe/a-NiFeOOH@NiMo	133.2 <sup>b</sup>	11	Fe-Co-CO <sub>3</sub> -OH	228	17
FeP/Ni <sub>2</sub> P	154	18	FeCo-Ni <sub>3</sub> S <sub>4</sub>	230 <sup>g</sup>	60
Gr-CNTs-Sn <sub>4</sub> P <sub>3</sub>	169 <sup>c</sup>	12	Ni/CeO <sub>2</sub> @N-CNFs	230	42
WCoSe/WCo <sub>3</sub> O <sub>4</sub>	175	78	NiMoB hollow foam	230	8
act-modified-ZIF-67	175	114	Co(OH) <sub>2</sub> /NiP <sub>x</sub>	236	103
NiFeV nf	181	127	Co <sub>3</sub> O <sub>4</sub>	236	29
Zn-Fe/Mn@Mn-FeP	184 <sup>d</sup>	28	IronCE10s	239.5	26
NiFe LDH	186	25	Co <sub>3-x</sub> O <sub>4</sub> /NiO	240	36
<sup>1</sup> M NaOH Fe <sub>60</sub> (CoNi) <sub>30</sub> Cr <sub>10</sub> activated	187	123	CoN@NC	240	106
Fe-CoP	190	85	S-FeOOH	244	24
NiFeLa LDH/v-MXene	191	57	Ag@NiFe LDH	246	54
Ce-NiFe	195	47	Fe <sub>2</sub> P-CoP/CeO <sub>2</sub>	248	101
Co <sub>0.21</sub> Fe <sub>0.28</sub> (OH)F	195	130	NiP <sub>2</sub> /NbP@CNTs	248.2 <sup>h</sup>	96
KT-Ni(0)@Ni(II)-TPA	197	112	CoP/FeOOH <sup>Electrolyte NA</sup>	250	104
(Ni-Fe) <sub>S<sub>x</sub></sub> /NiFe(OH) <sub>y</sub>	199	69	Ni/MoO <sub>2</sub> @CN	250	15
FeNiOH	200	44	e-FeCoNiCu-P	250	89
Fe@Co/Se <sub>2</sub>	200	77	Ce@NiCo LDH	250 <sup>i</sup>	55
NiFeB	201	126	C/O-FeNi/FeF <sub>2</sub>	253	131
S-NiFeP-10	201	91	Co/Mo <sub>2</sub> C@C	254	118
NiFe LDH <sup>activated</sup>	201	51	NiFe based	255	52
Ni <sub>3</sub> S <sub>2</sub> /FeNi <sub>2</sub> S <sub>4</sub>	201	66	MoSe <sub>2</sub> @NiCo <sub>2</sub> Se <sub>4</sub>	255	76
Ni <sub>5</sub> P <sub>4</sub> @FeP	205	90	NiCoFe-P/C	257 <sup>j</sup>	93
CoNiFe-OH	207	46	NiCoP	259	83
Co <sub>2</sub> P/Mo <sub>2</sub> C@NC	209	121	P-CoMoO <sub>4</sub>	260 <sup>k</sup>	40
FeOOH@NiFe LDH	210	53	CuNCO <sub>3</sub>	260	107
OR-NiOOH	213	38	Ni <sub>3</sub> Fe <sub>0.75</sub> V <sub>0.25</sub> /Ni <sub>3</sub> Fe <sub>0.75</sub> V <sub>0.25</sub> N	260 <sup>l</sup>	129
CoNiCuMnAl@C	215	124	FeCoS <sub>x</sub> -PBA	266	70
Fe <sub>2</sub> P-WO <sub>2.92</sub>	215	102	NiFe-VO <sub>x</sub>	267	128
MH-TMO	~216	1g	Sn-Ni <sub>3</sub> S <sub>2</sub>	267 <sup>m</sup>	14
Ni <sub>2</sub> P-Fe <sub>2</sub> P	218	19	Hea-d48h	270 <sup>n</sup>	125
Mo <sub>2</sub> C-CoO@NC	222	120	Fe-NiS-NiS <sub>2</sub>	270 <sup>o</sup>	62
Fe-VSB/NiPO-500	~227 <sup>e</sup>	105	CoP-NC@NiFeP	270 <sup>p</sup>	98

<sup>a</sup>  $\eta$ : overpotential; Ref.: references; NA: not applicable; c-NiFe/a-NiFeOOH@NiMo: crystalline-NiFe/amorphous-NiFeOOH@NiMo; e-FeCoNiCu-P: electrochemically etched FeCoNiCu-P; CNTs: carbon nanotubes; LDH: layered double hydroxide; VSB/NiPO: nickel phosphate microprism, where the microprism is mainly composed of Versailles-Santa Barbara-5, which is a kind of nickel phosphate molecular sieve having the chemical formula of Ni<sub>20</sub>[(OH)<sub>12</sub>(H<sub>2</sub>O)<sub>6</sub>][[(HPO<sub>4</sub>)<sub>8</sub>(PO<sub>4</sub>)<sub>4</sub>]-12H<sub>2</sub>O]; KT-Ni(0)@Ni(II)-TPA: a terephthalic acid (TPA)-regulated etching strategy is used for the preparation of a karst topography (KT) featured electrode containing core-shell structured Ni(0)@Ni(II)-TPA; LSC/LSCO: La<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3- $\delta$</sub> ; MH-TMO: mesoporous and heterostructured transition metal oxides; hea-d48h: it is a high-entropy alloy (hea), which is de-alloyed for 48 h, where the Ni<sub>30</sub>Co<sub>30</sub>Cr<sub>10</sub>Fe<sub>10</sub>Al<sub>18</sub>W<sub>2</sub> high-entropy alloy comprises FCC and ordered aluminum-enriched BCC phases, while three dimensional porous architecture is constructed by de-alloying (selective etching of the BCC phase) the high-entropy alloy for 48 h; N-CNFs: N-doped carbon nanofibers; act-modified-ZIF-67: activated modified Co-based zeolitic imidazolate framework; NiFeV nf: NiFeV nanofibers; IronCE10s: the catalyst was prepared on an iron substrate by applying pulsed potentials for 10 seconds, where the substrate was used as a counter electrode; FeCoS<sub>x</sub>-PBA: FeCoS embedded in a Prussian blue analogue hetero-nanoframes; Gr: graphene. <sup>b</sup> 133.2 mV at  $20 \text{ mA cm}^{-2}$ . <sup>c</sup> 169 mV at  $20 \text{ mA cm}^{-2}$ . <sup>d</sup> 184 mV at  $20 \text{ mA cm}^{-2}$ . <sup>e</sup> ~227 mV at  $50 \text{ mA cm}^{-2}$ . <sup>f</sup> 227 mV at  $50 \text{ mA cm}^{-2}$ . <sup>g</sup> 230 mV at  $20 \text{ mA cm}^{-2}$ . <sup>h</sup> 248.2 mV at  $20 \text{ mA cm}^{-2}$ . <sup>i</sup> 250 mV at  $50 \text{ mA cm}^{-2}$ . <sup>j</sup> 257 mV at  $100 \text{ mA cm}^{-2}$ . <sup>k</sup> 260 mV at  $20 \text{ mA cm}^{-2}$ . <sup>l</sup> 260 mV at  $50 \text{ mA cm}^{-2}$ . <sup>m</sup> 267 mV at  $100 \text{ mA cm}^{-2}$ . <sup>n</sup> 270 mV at  $50 \text{ mA cm}^{-2}$ . <sup>o</sup> 270 mV at  $50 \text{ mA cm}^{-2}$ . <sup>p</sup> 270 mV at  $50 \text{ mA cm}^{-2}$ .



hydroxide nanosheets as shells, which are vertically grown on the  $V_3O_7$  nanofiber as the core. It exhibits a heterointerface between NiFeV hydroxide and  $V_3O_7$ . In the high-resolution XPS

spectra, the Fe 2p peak of NiFeV nanofibers exhibits a slight positive shift when compared to that of NiFeV and NiFe, suggesting a modified electronic structure in NiFeV nanofibers with the formation of high valence Fe ions ( $Fe > 3+$ ), possibly due to the partial transfer of electrons from Fe to V. It contains  $V^{3+}$ ,  $V^{4+}$ , and  $V^{5+}$ . In contrast, the NiFeV nanofibers exhibit a higher amount of low oxidation state vanadium ( $V^{3+}$ ), when compared to that of NiFeV, suggesting the more partial transfer of electrons to the V in NiFeV nanofiber rather than in NiFeV, possibly due to the interfacial atom-substitution strategy. For the OER in 1 M KOH, it affords an  $\eta$  of 181 mV at  $10 \text{ mA cm}^{-2}$ , suggesting its very high activity.

Fabrication of NiFe-based vanadates with a moderate heterophase by a facile co-precipitation method could create abundant oxygen vacancies, enhance the conductivity, and generate hydroxide as active species by surface reconstruction during the OER, which could enhance the performance for the OER. Shao *et al.*<sup>128</sup> observed that NiFe- $VO_x$  exhibits enhanced activity and stability for the OER. It was synthesized by a facile co-precipitation method. NiFe- $VO_x$  exhibits higher activity and lower charge transfer resistance for the OER than NiCo- $VO_x$  and CoFe- $VO_x$ . NiFe- $VO_x$  exhibits a moderate heterophase, comprising both crystalline and amorphous structures. It contains  $Ni_2FeV_3O_{11}$  and  $Ni_2FeVO_6$  phases. It contains V, Fe, Ni, and O, which are homogeneously distributed. It contains abundant oxygen vacancies. It possesses nanoparticle morphology, which is further composed of small nanosheets. It exhibits the formation of hydroxide, possibly NiFe hydroxide, as an active species during the OER.

Fabrication of the  $Ni_3Fe_{0.75}V_{0.25}/Ni_3Fe_{0.75}V_{0.25}N$  heterojunction could modify the electronic structure, enhance the conductivity, and that could enhance the performance for the HER and OER, while it could generate a cmetal(oxy) hydroxide layer as active species by surface reconstruction during the OER, and that could enhance the performance for the OER. Lu *et al.*<sup>129</sup> observed that  $Ni_3Fe_{0.75}V_{0.25}/Ni_3Fe_{0.75}V_{0.25}N$  exhibits enhanced activity and stability for the HER and OER. It was synthesized by stirring followed by hydrothermal treatment followed by calcination at  $500 \text{ }^\circ\text{C}$  for 8 h in an  $NH_3$  atmosphere.  $Ni_3Fe_{0.75}V_{0.25}/Ni_3Fe_{0.75}V_{0.25}N$  exhibits higher activity and lower charge transfer resistance for the HER and OER than  $Ni_3FeN$ ,  $Ni_3Fe_{0.75}V_{0.25}N$ , and  $Ni_3Fe/Ni_3FeN$ . It is an  $Ni_3Fe_{0.75}V_{0.25}/Ni_3Fe_{0.75}V_{0.25}N$  heterojunction, while it contains  $Ni_3FeN$  and  $Ni_3Fe$  phases, where V is incorporated in both phases. It exhibits a heterointerface. It contains V, Fe, Ni, and N, which are homogeneously distributed. It exhibits surface reconstruction during the OER, where a thin amorphous NiFeOOH layer is formed on the surface of the  $Ni_3Fe_{0.75}V_{0.25}/Ni_3Fe_{0.75}V_{0.25}N$  heterojunction.

Fabrication of hybrid metal hydroxyl fluorides ( $Co_{0.21}Fe_{0.28}(\text{OH})\text{F}$ ) could modify the electronic structure, generate a larger  $Co^{2+}/Co^{3+}$  ratio, provide optimal adsorption energy with intermediates, enhance the conductivity, expose abundant active sites, and that could enhance the performance for the HER and OER. Li *et al.*<sup>130</sup> observed that  $Co_{0.21}Fe_{0.28}(\text{OH})\text{F}$  exhibits enhanced activity and stability for the

**Table 7** Overpotential ( $\eta$  (Part 2:  $\eta$  from 271.7 to 500 mV)) to achieve  $10 \text{ mA cm}^{-2}$  for the oxygen evolution reaction (OER) of various reported noble metal-free electrocatalysts in 1 M KOH alkaline electrolyte, where the electrolyte other than 1 M KOH is indicated on the electrocatalyst. ( $\eta$  values to achieve greater than  $10 \text{ mA cm}^{-2}$  are indicated on the  $\eta$ , which are described in the footnote of this table)<sup>a</sup>

OER electrocatalysts	$\eta$ at $10 \text{ mA cm}^{-2}$ (mV)	Ref.
c-CoFeP/a-CoFe LDH	271.7 <sup>b</sup>	56
act-Ni-CoP/Co <sub>2</sub> P@NC	272	97
MoO <sub>2</sub> /Co	280	30
f-Ni <sub>0.1</sub> Co <sub>0.9</sub> O <sub>x</sub>	282	35
Co <sub>2</sub> N <sub>0.67</sub> /CoMoO <sub>4</sub>	283	20
SS-500-AO	284.3	79
Cu <sub>3</sub> P-Cu <sub>2</sub> O/NPC	286	100
Ni-FePS <sub>3</sub>	287	71
Mn <sub>1</sub> Ni <sub>1</sub> Co <sub>1</sub> -P	289	10
Co <sub>3</sub> O <sub>4</sub> SS Mesh/ZnO <sup>0.1 M KOH</sup>	290	37
1T Co-WS <sub>2</sub> /NiTe <sub>2</sub> /Ni	290 <sup>c</sup>	73
Fe/Mo <sub>2</sub> C-NC	293 <sup>d</sup>	117
Co-Mn-Co <sub>3</sub> -OH	294 <sup>e</sup>	48
SAE <sub>OER</sub> -ECT-NiSi	296 <sup>f</sup>	132
WO <sub>3</sub> @F <sub>0.1</sub> -C	298	27
NiFe-(OOH)-based <sup>0.1 M KOH</sup>	300 <sup>g</sup>	50
Mn <sub>6</sub> -CoO	301 <sup>h</sup>	31
LSC-N-GQDs-MoSe <sub>2</sub>	302	80
NiP	305	88
Defect-FeOOH <sup>activated</sup>	307	49
Annealed $\alpha$ -Ni(OH) <sub>2</sub>	310	43
Co-Ni <sub>3</sub> S <sub>2</sub>	310 <sup>i</sup>	59
Co <sub>x</sub> P/NC-melamine	312	99
Ni <sub>x</sub> S <sub>y</sub> @MnO <sub>x</sub> H <sub>y</sub>	326 <sup>j</sup>	15
S-Co <sub>2</sub> P@Ni <sub>2</sub> P	~330 <sup>k</sup>	87
Fe <sub>2</sub> P/Co@NPC	331	6e
CuS-Ni <sub>3</sub> S <sub>2</sub> /CuNi	337 <sup>l</sup>	22
C-Ni <sub>1-x</sub> O/3D printed Ni	~340 <sup>m</sup>	16
CoNiP	~350 <sup>n</sup>	84
Ni <sub>3</sub> S <sub>2</sub> -MoS <sub>2</sub>	~350 <sup>o</sup>	65
Co-CoO/GO	372 <sup>p</sup>	41
NiS/MoS <sub>2</sub>	~410 <sup>q</sup>	64
Co-Ni <sub>3</sub> S <sub>2</sub> <sup>1 M NaOH</sup>	500 <sup>r</sup>	58

<sup>a</sup>  $\eta$ : overpotential; c-CoFeP/a-CoFe LDH: crystalline CoFeP decorated amorphous CoFe LDH; act-Ni-CoP/Co<sub>2</sub>P@NC: activated Ni-CoP/Co<sub>2</sub>P@NC; SS-500-AO: it is an electrocatalyst on SUS304 stainless steel, where the catalyst was prepared by selenization followed by heat treatment followed by electrochemical oxidation; SAE<sub>OER</sub>-ECT-NiSi: NiSi is subjected to ECT followed by SAE<sub>OER</sub>, where ECT is an electrochemical tuning process comprising lithiation and rapid delithiation of NiSi, while SAE<sub>OER</sub> is a self-adaptive evolution that involves conducting multiple linear sweep voltammetry on ECT-NiSi under OER conditions; N-GQDs: N-doped graphene quantum dots; LSC/LSCO: La<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3- $\delta$</sub> ; Co<sub>x</sub>P/NC-melamine: Co<sub>x</sub>P/NC was prepared through a melamine assisted synthesis route. <sup>b</sup> 271.7 mV at  $100 \text{ mA cm}^{-2}$ . <sup>c</sup> 290 mV at  $30 \text{ mA cm}^{-2}$ . <sup>d</sup> 293 mV at  $100 \text{ mA cm}^{-2}$ . <sup>e</sup> 294 mV at  $30 \text{ mA cm}^{-2}$ . <sup>f</sup> 296 mV at  $100 \text{ mA cm}^{-2}$ . <sup>g</sup> 300 mV at  $\sim 701 \text{ A g}^{-1}$ . <sup>h</sup> 301 mV at  $50 \text{ mA cm}^{-2}$ . <sup>i</sup> 310 mV at  $50 \text{ mA cm}^{-2}$ . <sup>j</sup> 326 mV at  $100 \text{ mA cm}^{-2}$ . <sup>k</sup>  $\sim 330 \text{ mV}$  at  $100 \text{ mA cm}^{-2}$ . <sup>l</sup> 337 mV at  $100 \text{ mA cm}^{-2}$ . <sup>m</sup>  $\sim 340 \text{ mV}$  at  $100 \text{ mA cm}^{-2}$ . <sup>n</sup>  $\sim 350 \text{ mV}$  at  $20 \text{ mA cm}^{-2}$ . <sup>o</sup>  $\sim 350 \text{ mV}$  at  $50 \text{ mA cm}^{-2}$ . <sup>p</sup> 372 mV at  $50 \text{ mA cm}^{-2}$ . <sup>q</sup>  $\sim 410 \text{ mV}$  at  $100 \text{ mA cm}^{-2}$ . <sup>r</sup> 500 mV at  $100 \text{ mA cm}^{-2}$ .



HER and OER. It was obtained on pretreated Ni foam by one-step hydrothermal treatment at 120 °C for 3 h.  $\text{Co}_{0.21}\text{Fe}_{0.28}(\text{OH})\text{F}$  exhibits higher activity, higher electrochemical surface area, and lower charge transfer resistance for the OER than  $\text{Co}_{0.14}\text{Fe}_{0.78}(\text{OH})\text{F}$  and  $\text{Co}_{0.41}\text{Fe}_{0.14}(\text{OH})\text{F}$ . In comparison, it exhibits higher activity for the HER than

$\text{Co}_{0.14}\text{Fe}_{0.78}(\text{OH})\text{F}$  and  $\text{Co}_{0.41}\text{Fe}_{0.14}(\text{OH})\text{F}$ . It is a hybrid metal hydroxyl fluoride ( $\text{Co}_{0.21}\text{Fe}_{0.28}(\text{OH})\text{F}$ ), containing  $\text{FeO}(\text{OH})$ ,  $\text{Co}(\text{OH})\text{F}$ , and  $\text{Ni}(\text{OH})_2$  phases. It contains Fe, Co, O, F, and Ni, which are homogeneously distributed, where a small amount of Ni comes from the Ni foam substrate. The  $\text{Co}^{2+}/\text{Co}^{3+}$  ratio is 1.94 for  $\text{Co}_{0.21}\text{Fe}_{0.28}(\text{OH})\text{F}$ , which is larger than

**Table 8** Long-term stability (Part 1: 40 h to 1200 h of duration) of various reported noble metal-free electrocatalysts for the oxygen evolution reaction (OER) in 1 M KOH alkaline electrolyte<sup>a</sup>

OER electrocatalysts	Chr amp	Chr pot	Dur (h)	Remark after the stability test	Ref.
NiFeLa LDH/v-MXene	NA	Yes	1200	Negligible decay at a CD of 100 mA cm <sup>-2</sup>	57
FeCo-Ni <sub>3</sub> S <sub>4</sub>	NA	Yes	360	22 mV decay at a CD of 20 mA cm <sup>-2</sup>	60
Ni/MoO <sub>2</sub> @CN	NA	Yes	200	Negligible decay at a CD of 1000 mA cm <sup>-2</sup>	15
NiFe LDH	NA	Yes	192	Reasonable stability at a CD of 100 mA cm <sup>-2</sup>	25
SS-500-AO	NA	Yes	160	Negligible decay at a CD of 10 mA cm <sup>-2</sup>	79
Ni <sub>x</sub> S <sub>y</sub> @MnO <sub>x</sub> H <sub>y</sub>	NA	Yes	150	Reasonable stability at a CD of 100 mA cm <sup>-2</sup>	68
Co <sub>0.21</sub> Fe <sub>0.28</sub> (OH)F	NA	Yes	120	Negligible decay at a CD of 20 mA cm <sup>-2</sup>	130
Gr-CNTs-Sn <sub>4</sub> P <sub>3</sub>	NA	Yes	105	~96% retention	12
FeOOH@NiFe LDH	NA	Yes	100	Negligible decay	53
NiFeB	NA	Yes	100	Reasonable stability at a CD of 500 mA cm <sup>-2</sup>	126
Ce-NiFe	NA	Yes	100	Reasonable stability at a CD of 1000 mA cm <sup>-2</sup>	47
S-FeOOH	NA	Yes	100	Negligible decay at a CD of 20 mA cm <sup>-2</sup>	24
Ni <sub>5</sub> P <sub>4</sub> @FeP	NA	Yes	100	Negligible decay at a CD of 100 mA cm <sup>-2</sup>	90
OR-NiOOH	NA	Yes	100	Reasonable stability at a CD of 1000 A m <sup>-2</sup>	38
Fe-VSB/NiPO-500	NA	Yes	100	98.2% retention at a CD of 50 mA cm <sup>-2</sup>	105
MH-TMO	NA	Yes	100	Negligible decay at a CD of 10 mA cm <sup>-2</sup>	1g
act-modified-ZIF-67	NA	Yes	100	96.6% retention at a CD of 100 mA cm <sup>-2</sup>	114
Cu <sub>3</sub> P-Cu <sub>2</sub> O/NPC	Yes	NA	90	Negligible decay	100
Zn-Fe/Mn@Mn-FeP	NA	Yes	80	Negligible decay at a CD of 50 mA cm <sup>-2</sup>	28
Co <sub>3-x</sub> O <sub>4</sub> /NiO	Yes	NA	60	Reasonable stability at 1.47 V	36
CoNiFe-OH	NA	Yes	60	Negligible decay at a CD of 10 mA cm <sup>-2</sup>	46
Fe <sub>2</sub> P-WO <sub>2.92</sub>	NA	Yes	60	93% retention at a CD of 100 mA cm <sup>-2</sup>	102
Mn <sub>6</sub> -CoO	Yes	NA	~60	85.2% retention	31
Hea-d48h	Yes	NA	60	Negligible decay	125
Sn-Ni <sub>3</sub> S <sub>2</sub>	Yes	NA	60	Negligible decay at an η of 438 mV	14
Defect-FeOOH <sup>activated</sup>	NA	Yes	55	Reasonable stability at a CD of 10 mA cm <sup>-2</sup>	49
act-Ni-CoP/Co <sub>2</sub> P@NC	Yes	NA	50	Negligible decay	97
WCoSe/WCo <sub>3</sub> O <sub>4</sub>	NA	Yes	50	Reasonable stability at a CD of 100 mA cm <sup>-2</sup>	78
Ni <sub>3</sub> S <sub>2</sub> /FeNi <sub>2</sub> S <sub>4</sub>	Yes	NA	50	Negligible decay	66
(Ni-Fe) <sub>x</sub> /NiFe(OH) <sub>y</sub>	NA	Yes	50	Negligible decay at a CD of 100 mA cm <sup>-2</sup>	69
CuNCo <sub>3</sub>	Yes	NA	48	86% retention	107
Ni-FePS <sub>3</sub>	NA	Yes	48	Negligible decay at a CD of 10 mA cm <sup>-2</sup>	71
Co/Mo <sub>2</sub> C@C	Yes	NA	48	92.3% retention at an η of 254 mV	118
Mn <sub>1</sub> Ni <sub>1</sub> Co <sub>1</sub> P	Yes	NA	48	Reasonable stability	10
Ni <sub>2</sub> P-Fe <sub>2</sub> P	NA	Yes	48	Negligible decay at a CD of 100/500 mA cm <sup>-2</sup>	19
Co <sub>2</sub> N <sub>0.67</sub> /CoMoO <sub>4</sub>	NA	Yes	>45	Reasonable stability at a CD of 100 mA cm <sup>-2</sup>	20
KT-Ni(0)@Ni(II)-TPA	Yes	NA	>45	Reasonable stability at an η of 206 mV to 370 mV	112
NiFeV nf	NA	Yes	>40	Reasonable stability	127
NiFe based	NA	Yes	40	Reasonable stability at a CD of 5 mA cm <sup>-2</sup>	52
P-CoMoO <sub>4</sub>	NA	Yes	40	Negligible decay at a CD of 50 mA cm <sup>-2</sup>	40
Fe,Ce-Ni <sub>x</sub> S <sub>y</sub>	NA	Yes	40	Reasonable stability at a CD of 10 mA cm <sup>-2</sup>	61
CoP-NC@NiFeP	NA	Yes	40	Negligible decay at a CD of 50 mA cm <sup>-2</sup>	98

<sup>a</sup> η: overpotential; Ref.: references; Dur: duration of the stability test; Chr pot: chronopotentiometry; Chr amp: chronoamperometry; NA: not applicable; CD: current density; CNTs: carbon nanotubes; LDH: layered double hydroxide; VSB/NiPO: nickel phosphate microprism, where the microprism is mainly composed of Versailles-Santa Barbara-5, which is a kind of nickel phosphate molecular sieve having the chemical formula of Ni<sub>20</sub>[(OH)<sub>12</sub>(H<sub>2</sub>O)<sub>6</sub>][(HPO<sub>4</sub>)<sub>8</sub>(PO<sub>4</sub>)<sub>4</sub>]·12H<sub>2</sub>O; KT-Ni(0)@Ni(II)-TPA: a terephthalic acid (TPA)-regulated etching strategy is used for the preparation of a karst topography (KT) featured electrode containing core-shell structured Ni(0)@Ni(II)-TPA; MH-TMO: mesoporous and heterostructured transition metal oxides; hea-d48h: it is a high-entropy alloy (hea), which is de-alloyed for 48 h, where the Ni<sub>30</sub>Co<sub>30</sub>Cr<sub>10</sub>Fe<sub>10</sub>Al<sub>18</sub>W<sub>2</sub> high-entropy alloy comprises FCC and ordered aluminum-enriched BCC phases, while three dimensional porous architecture is constructed by de-alloying (selective etching of the BCC phase) the high-entropy alloy for 48 h; act-Ni-CoP/Co<sub>2</sub>P@NC: activated Ni-CoP/Co<sub>2</sub>P@NC; act-modified-ZIF-67: activated modified Co-based zeolitic imidazolate framework; NiFeV nf: NiFeV nanofibers; SS-500-AO: it is an electrocatalyst on SUS304 stainless steel, where the catalyst was prepared by selenization followed by heat treatment followed by electrochemical oxidation; Gr: graphene.



that of 1.38 for  $\text{Co}_{0.14}\text{Fe}_{0.78}(\text{OH})\text{F}$ , and 1.30 for  $\text{Co}_{0.41}\text{Fe}_{0.14}(\text{OH})\text{F}$ , suggesting the exposure of more  $\text{Co}^{2+}$  ions due to the presence of an optimal proportion of Co and Fe in  $\text{Co}_{0.21}\text{Fe}_{0.28}(\text{OH})\text{F}$ . It exhibits the formation of metal hydroxide (metal(oxy)hydroxide or metal hydroxide) as active species by surface reconstruction during the OER. It possesses nanosheet array morphology. For the OER in 1 M KOH, it affords an  $\eta$  of 195 mV at  $10 \text{ mA cm}^{-2}$ , suggesting its very high activity, while it undergoes negligible decay at  $20 \text{ mA cm}^{-2}$  for 120 h, suggesting its very high stability. For the HER in 1 M KOH, it affords an  $\eta$  of  $-73 \text{ mV}$  at  $-10 \text{ mA cm}^{-2}$ , suggesting its very high activity. For overall water splitting in 1 M KOH,  $\text{Co}_{0.21}\text{Fe}_{0.28}(\text{OH})\text{F}/\text{Co}_{0.21}\text{Fe}_{0.28}(\text{OH})\text{F}$  affords

a potential of 1.53 V at  $10 \text{ mA cm}^{-2}$ , suggesting its high activity.

Fabrication of carbon-confined iron–nickel alloy/iron fluoride could modify the electronic structure, enhance the conductivity, expose abundant active sites, and enhance the performance of the OER. Li *et al.*<sup>131</sup> observed that C/O-FeNi/FeF<sub>2</sub> exhibits enhanced activity and stability for the OER. It was synthesized by hydrothermal treatment (for the formation of the Fe<sub>2</sub>Ni MIL MOF) followed by carbonization at 800 °C for 1 h in N<sub>2</sub> (for the formation of FeNi-800 °C) followed by fluorination at 450 °C for 2 h in N<sub>2</sub> (for the formation of C/O-FeNi/FeF<sub>2</sub>). C/O-FeNi/FeF<sub>2</sub> exhibits higher activity, higher electrochemical surface area, and lower charge transfer resistance for

**Table 9** Long-term stability (Part 2: 4 h to 35 h of duration) of various reported noble metal-free electrocatalysts for the oxygen evolution reaction (OER) in 1 M KOH alkaline electrolyte, where electrolytes other than 1 M KOH are indicated on the electrocatalyst<sup>a</sup>

OER electrocatalysts	Chr amp	Chr pot	Dur (h)	Remark after the stability test	Ref.
SAE <sub>OER</sub> -ECT-NiSi	Yes	NA	35	Negligible decay at an $\eta$ of 470 mV	132
NiCoFe-P/C	Yes	NA	34	Negligible decay	93
NiP <sub>2</sub> /NbP@CNTs	Yes	NA	33	~88.2% retention at an $\eta$ of 274.1 mV	96
Co <sub>2</sub> P/Mo <sub>2</sub> C@NC	Yes	NA	30	Negligible decay	121
Ni <sub>3</sub> Fe <sub>0.75</sub> V <sub>0.25</sub> /Ni <sub>3</sub> Fe <sub>0.75</sub> V <sub>0.25</sub> N	Yes	NA	30	Reasonable stability	129
Fe <sub>2</sub> P-CoP/CeO <sub>2</sub>	Yes	NA	30	Negligible decay	101
Co-Ni <sub>3</sub> S <sub>2</sub>	Yes	NA	30	Negligible decay at an $\eta$ of 465 mV	59
Fe-CoP	NA	Yes	30	Negligible decay at a CD of $1000 \text{ mA cm}^{-2}$	85
Annealed $\alpha$ -Ni(OH) <sub>2</sub>	NA	Yes	26	Negligible decay at a CD of $10 \text{ mA cm}^{-2}$	43
CoN@NC	NA	Yes	25	Reasonable stability at a CD of $10 \text{ mA cm}^{-2}$	106
WO <sub>3</sub> @F <sub>0.1</sub> -C	NA	Yes	24	Negligible decay	27
f-Ni <sub>0.1</sub> Co <sub>0.9</sub> O <sub>x</sub>	Yes	NA	24	Reasonable stability at a potential of 1.53 V	35
CoNiCuMnAl@C	NA	Yes	24	Negligible decay at a CD of $10 \text{ mA cm}^{-2}$	124
1T Co-WS <sub>2</sub> /NiTe <sub>2</sub> /Ni	NA	Yes	24	Reasonable stability at a CD of $50 \text{ mA cm}^{-2}$	73
S-NiFeP-10	Yes	NA	24	Reasonable stability	91
Co-Ni <sub>3</sub> S <sub>2</sub> 1 M NaOH	NA	Yes	24	Negligible decay at a CD of $50 \text{ mA cm}^{-2}$	58
Fe/Mo <sub>2</sub> C-NC	Yes	NA	24	Reasonable stability	117
Ce@NiCo LDH	Yes	NA	24	Reasonable stability at a potential of 1.55 V	55
FeP/Ni <sub>2</sub> P	NA	Yes	24	Negligible decay at $100 \text{ mA cm}^{-2}$	18
FeNiOH	Yes	NA	20	Negligible decay at a potential of 1.46 V	44
CoP/FeOOH <sup>Electrolyte NA</sup>	NA	Yes	20	Reasonable stability at a CD of $10 \text{ mA cm}^{-2}$	104
S-Co <sub>2</sub> P@Ni <sub>2</sub> P	Yes	NA	20	Negligible decay	87
Fe@Co/Se <sub>2</sub>	NA	Yes	20	Negligible decay at a CD of $10 \text{ mA cm}^{-2}$	77
Ag@NiFe LDH	Yes	NA	>19	Reasonable stability	54
Co-Mn-CO <sub>3</sub> -OH	NA	Yes	18	Negligible decay at a CD of $50 \text{ mA cm}^{-2}$	48
C/O-FeNi/FeF <sub>2</sub>	Yes	NA	16	Reasonable stability	131
Fe <sub>2</sub> P/Co@NPC	NA	Yes	>16	Reasonable stability at a CD of $10 \text{ mA cm}^{-2}$	6e
Co <sub>3</sub> O <sub>4</sub>	NA	Yes	>15	Negligible decay at a CD of $100 \text{ mA cm}^{-2}$	29
CuS-Ni <sub>3</sub> S <sub>2</sub> /CuNi	NA	Yes	15	Negligible decay at a CD of $100 \text{ mA cm}^{-2}$	22
NiFe-VO <sub>x</sub>	NA	Yes	12	24.2 mV decay at a CD of $10 \text{ mA cm}^{-2}$	128
Co-CoO/GO	Yes	NA	12	93% retention at a potential of 1.71 V	41
NiCoP	Yes	NA	12	99% retention at an $\eta$ of 259 mV	83
Fe-NiS-NiS <sub>2</sub>	Yes	NA	12	Reasonable stability at an $\eta$ of 270 mV	62
Co(OH) <sub>2</sub> /NiP <sub>x</sub>	NA	Yes	>10	Reasonable stability at a CD of $10 \text{ mA cm}^{-2}$	103
FeCoS <sub>x</sub> -PBA	Yes	NA	10	98.3% retention	70
Ni/CeO <sub>2</sub> @N-CNFs	Yes	NA	>10	Negligible decay	42
Co <sub>3</sub> O <sub>4</sub> SS Mesh/ZnO <sup>0.1 M KOH</sup>	Yes	NA	7	Reasonable stability	37
Co <sub>x</sub> P/NC-melamine	NA	Yes	4	Reasonable stability at a CD of $10 \text{ mA cm}^{-2}$	99

<sup>a</sup>  $\eta$ : overpotential; Ref.: references; Dur: duration of the stability test; Chr pot: chronopotentiometry; Chr amp: chronoamperometry; NA: not applicable; CD: current density; SAE<sub>OER</sub>-ECT-NiSi: NiSi is subjected to ECT followed by SAE<sub>OER</sub>, where ECT is an electrochemical tuning process comprising lithiation and rapid delithiation of NiSi, while SAE<sub>OER</sub> is a self-adaptive evolution that involves conducting multiple linear sweep voltammetry on ECT-NiSi under OER conditions; CNTs: carbon nanotubes; LDH: layered double hydroxide; FeCoS<sub>x</sub>-PBA: FeCoS embedded in Prussian blue analogue hetero-nanoframes; N-CNFs: N-doped carbon nanofibers; Co<sub>x</sub>P/NC-melamine: Co<sub>x</sub>P/NC was prepared through a melamine assisted synthesis route.



the OER than FeNi-800 °C and Fe<sub>2</sub>Ni MIL MOF. It is composed of oxygen-doped FeNi/FeF<sub>2</sub>, confined by carbon. In the high-resolution XPS spectra, the Fe 2p peak corresponding to Fe<sup>2+</sup> of C/O-FeNi/FeF<sub>2</sub> exhibits a slight positive shift when compared to that of FeNi-800 °C, suggesting a modified electronic structure. It could exhibit the formation of metal(oxy) hydroxide by surface reconstruction during the OER.

An electrochemical tuning process comprising lithiation and rapid delithiation of the nanostructured NiSi could form a core-shell structure. In contrast, the subsequent electrochemical activation could increase the oxygen vacancies, enhance the conductivity, provide optimal adsorption energy with intermediates, increase the electrochemical surface area, and that could enhance the performance of the HER and OER. Chang *et al.*<sup>132</sup> observed that SAE<sub>HER</sub>-ECT-NiSi

exhibits enhanced activity and stability for the HER, while SAE<sub>OER</sub>-ECT-NiSi exhibits enhanced activity and stability for the OER. In SAE<sub>HER</sub>-ECT-NiSi, the NiSi nanowires prepared by CVD are subjected to ECT followed by SAE<sub>HER</sub>, where ECT is an electrochemical tuning process comprising lithiation and rapid delithiation of NiSi. At the same time, SAE<sub>HER</sub> is a self-adaptive evolution that involves conducting multiple linear sweep voltammetry on ECT-NiSi under HER conditions. In SAE<sub>OER</sub>-ECT-NiSi, the NiSi nanowires prepared by CVD are subjected to ECT followed by SAE<sub>OER</sub>, where ECT is an electrochemical tuning process comprising lithiation and rapid delithiation of NiSi. At the same time, SAE<sub>OER</sub> is a self-adaptive evolution that involves conducting multiple linear sweep voltammetry on ECT-NiSi under OER conditions. SAE<sub>HER</sub>-ECT-NiSi exhibits higher activity and lower charge

**Table 10** Durability of various reported noble metal-free electrocatalysts for the oxygen evolution reaction (OER) in 1 M KOH alkaline electrolyte, where the electrolyte other than 1 M KOH is indicated on the electrocatalyst<sup>a</sup>

OER electrocatalysts	Cycles of CV	Remark after the durability test	Ref.
Cu <sub>3</sub> P-Cu <sub>2</sub> O/NPC	20 000	Negligible decay at 150 mA cm <sup>-2</sup>	100
NiCoP	10 000	Negligible decay at 90 mA cm <sup>-2</sup>	83
Sn-Ni <sub>3</sub> S <sub>2</sub>	10 000	Negligible decay at 2000 mA cm <sup>-2</sup>	14
Ni <sub>x</sub> S <sub>y</sub> @MnO <sub>x</sub> H <sub>y</sub>	5000	Negligible decay at 500 mA cm <sup>-2</sup>	68
Gr-CNTs-Sn <sub>4</sub> P <sub>3</sub>	5000	Negligible decay at 200 mA cm <sup>-2</sup>	12
Mn <sub>1</sub> Ni <sub>1</sub> Co <sub>1</sub> -P	5000	Negligible decay at 10 mA cm <sup>-2</sup>	10
FeP/Ni <sub>2</sub> P	5000	Negligible decay at 1500 mA cm <sup>-2</sup>	18
CuS-Ni <sub>3</sub> S <sub>2</sub> /CuNi	5000	Negligible decay at 1000 mA cm <sup>-2</sup>	22
CoNiCuMnAl@C	3000	Negligible decay at 90 mA cm <sup>-2</sup>	124
FeCo-Ni <sub>3</sub> S <sub>4</sub>	3000	Negligible decay at 100 mA cm <sup>-2</sup>	60
Co <sub>2</sub> P/Mo <sub>2</sub> C@NC	3000	Negligible decay at 90 mA cm <sup>-2</sup>	121
Mn <sub>6</sub> -CoO	3000	13 mV decay	31
Co <sub>2</sub> N <sub>0.67</sub> /CoMoO <sub>4</sub>	3000	Negligible decay	20
Ni/CeO <sub>2</sub> @N-CNFs	3000	Negligible decay at 60 mA cm <sup>-2</sup>	42
Ni <sub>2</sub> P-Fe <sub>2</sub> P	3000	Negligible decay at 1000 mA cm <sup>-2</sup>	19
(Ni-Fe) <sub>x</sub> /NiFe(OH) <sub>y</sub>	3000	Negligible decay at 100 mA cm <sup>-2</sup>	69
c-NiFe/a-NiFeOOH@NiMo	2000	Negligible decay at 10 mA cm <sup>-2</sup>	11
Ni-FePS <sub>3</sub>	2000	Negligible decay at 100 mA cm <sup>-2</sup>	71
Fe@Co/Se <sub>2</sub>	2000	Negligible decay at 10 mA cm <sup>-2</sup>	77
Ni <sub>3</sub> S <sub>2</sub> /FeNi <sub>2</sub> S <sub>4</sub>	2000	Negligible decay at 300 mA cm <sup>-2</sup>	66
Mo <sub>2</sub> C-CoO@NC	2000	Negligible decay at 75 mA cm <sup>-2</sup>	120
FeOOH@NiFe LDH	1000	Negligible decay at 300 mA cm <sup>-2</sup>	53
C/O-FeNi/FeF <sub>2</sub>	1000	Negligible decay at 50 mA cm <sup>-2</sup>	131
f-Ni <sub>0.1</sub> Co <sub>0.9</sub> O <sub>x</sub>	1000	Slight decay at 100 mA cm <sup>-2</sup>	35
FeNiOH	1000	Negligible decay at 90 mA cm <sup>-2</sup>	44
Ni <sub>5</sub> P <sub>4</sub> @FeP	1000	Negligible decay at 350 mA cm <sup>-2</sup>	90
Co <sub>3</sub> O <sub>4</sub> SS Mesh/ZnO <sup>0.1 M KOH</sup>	1000	Negligible decay at 10 mA cm <sup>-2</sup>	37
CoP/FeOOH <sup>Electrolyte NA</sup>	1000	Slight decay at 90 mA cm <sup>-2</sup>	104
S-Co <sub>2</sub> P@Ni <sub>2</sub> P	1000	Negligible decay at 600 mA cm <sup>-2</sup>	87
S-NiFeP-10	1000	Negligible decay	91
Hea-d48h	1000	Negligible decay at 125 mA cm <sup>-2</sup>	125
Zn-Fe/Mn@Mn-FeP	1000	Negligible decay at 150 mA cm <sup>-2</sup>	28
Fe-NiS-NiS <sub>2</sub>	1000	Negligible decay at 350 mA cm <sup>-2</sup>	62
Fe,Ce-Ni <sub>x</sub> S <sub>y</sub>	1000	Negligible decay at 225 mA cm <sup>-2</sup>	61
Co/Mo <sub>2</sub> C@C	1000	Negligible decay at 10 mA cm <sup>-2</sup>	118
Co-Ni <sub>3</sub> S <sub>2</sub>	1000	Negligible decay at 1000 mA cm <sup>-2</sup>	59
NiMoB hollow foam	500	Negligible decay at 600 mA cm <sup>-2</sup>	8

<sup>a</sup> NA: not applicable; CNTs: carbon nanotubes; LDH: layered double hydroxide; N-CNFs: N-doped carbon nanofibers; c-NiFe/a-NiFeOOH@NiMo: crystalline-NiFe/amorphous-NiFeOOH@NiMo; hea-d48h: it is a high-entropy alloy (hea), which is de-alloyed for 48 h, where the Ni<sub>30</sub>Co<sub>30</sub>Cr<sub>10</sub>Fe<sub>10</sub>Al<sub>18</sub>W<sub>2</sub> high-entropy alloy comprises FCC and ordered aluminum-enriched BCC phases, while three dimensional porous architecture is constructed by de-alloying (selective etching of the BCC phase) the high-entropy alloy for 48 h; Gr: graphene.



transfer resistance for the HER than NiSi nanowires. SAE<sub>OER</sub>-ECT-NiSi exhibits higher activity, higher electrochemical surface area, and lower charge transfer resistance for the OER than NiSi nanowires. The NiSi with a core-shell structure is formed by the ECT process of the NiSi nanowires, where the intact core is surrounded by an amorphous shell dispersed with nanoparticles. The SAE<sub>HER</sub>-ECT-NiSi contains oxidized Ni, metallic Ni, oxidized Si, and metallic Si, which is almost similar to that of ECT-NiSi. In contrast, the self-adaptive evolution on ECT-NiSi under HER conditions increases the oxygen vacancies. In the high-resolution Ni 2p, Si 2p, and O 1s XPS spectra of SAE<sub>OER</sub>-ECT-NiSi, a considerable decrease in the metallic Ni and Si peak intensities, an increase in the oxidized Ni and Si peak intensities, and an increase in the peak intensity for oxygen vacancies are observed, when

compared to those of ECT-NiSi. At the same time, the formation of the Ni(OH)<sub>2</sub> phase is also observed in SAE<sub>OER</sub>-ECT-NiSi. Tables 1 and 2 provide the overpotential to achieve -10 mA cm<sup>-2</sup> for the HER of various reported noble metal-free electrocatalysts in alkaline electrolytes. Tables 3 and 4 provide the long-term stability of various reported noble metal-free electrocatalysts for the HER in alkaline electrolytes. Table 5 provides the durability of various reported noble metal-free electrocatalysts for the HER in alkaline electrolytes. Tables 6 and 7 provide the overpotential to achieve 10 mA cm<sup>-2</sup> for the OER of various reported noble metal-free electrocatalysts in alkaline electrolytes. Tables 8 and 9 provide the long-term stability of various reported noble metal-free electrocatalysts for the OER in alkaline electrolytes. Table 10 provides the durability of various

**Table 11** Potential (Part 1: potential from 1.42 to 1.55 V) to achieve 10 mA cm<sup>-2</sup> for overall water splitting of different kinds of reported non-noble metal bifunctional electrocatalysts in an alkaline electrolyte<sup>a</sup>

Bifunctional electrocatalysts for the HER and OER	Overall water splitting (V at 10 mA cm <sup>-2</sup> )	Electrolyte	Ref.
FeP/Ni <sub>2</sub> P	1.42	1 M KOH	18
NiMoB hollow foam	1.431	1 M KOH	8
c-NiFe/a-NiFeOOH@NiMo	1.45	1 M KOH	11
Ni-C hnsa	~1.45 <sup>b</sup>	1 M KOH	111
Sn-Ni <sub>3</sub> S <sub>2</sub>	1.46	1 M KOH	14
(Ni-Fe) <sub>2</sub> S <sub>4</sub> /NiFe(OH) <sub>y</sub>	1.46	1 M KOH	69
NiCoP	1.48	1 M KOH	83
NiFeLa LDH/v-MXene	1.48	1 M KOH	57
Mn <sub>1</sub> Ni <sub>1</sub> Co <sub>1</sub> -P	1.48	1 M KOH	10
Gr-CNTs-Sn <sub>4</sub> P <sub>3</sub>	1.482	1 M KOH	12
Co <sub>3</sub> O <sub>4</sub>	1.483	1 M KOH	29
<sup>nb</sup> Fe-VSB/NiPO-500 <sup>OER</sup> //VSB/NiPO <sup>HER</sup>	1.487	1 M KOH	105
MH-TMO	1.49	1 M KOH	1g
WCoSe/WCo <sub>3</sub> O <sub>4</sub>	1.49	1 M KOH	78
Fe-CoP	1.49	1 M KOH	85
<sup>nb</sup> c-CoFeP/a-CoFe LDH <sup>OER</sup> //c-CoMnP/a-CoMn LDH <sup>HER</sup>	1.498	1 M KOH	56
<sup>nb</sup> S-NiFeP-10 <sup>OER</sup> //S-NiFeP-20 <sup>HER</sup>	1.5	1 M KOH	91
NiS/MoS <sub>2</sub>	1.51	1 M KOH	64
NiP <sub>2</sub> /NbP@CNTs	1.51	1 M KOH	96
<sup>nb</sup> OR-NiOOH <sup>OER</sup> //HR-NiMoO@Ni <sup>HER</sup>	1.51	1 M KOH	38
Fe@Co/Se <sub>2</sub>	1.51	1 M KOH	77
<sup>nb</sup> act-modified-ZIF-67 <sup>OER</sup> //M-Co-CN <sup>HER</sup>	1.51	1 M KOH	114
Mn <sub>6</sub> -CoO	1.52	1 M KOH	31
S-Co <sub>2</sub> P@Ni <sub>2</sub> P	1.52	1 M KOH	87
Fe <sub>2</sub> P-CoP/CeO <sub>2</sub>	1.52	1 M KOH	101
1T Co-WS <sub>2</sub> /NiTe <sub>2</sub> /Ni	1.521	1 M KOH	73
Ni <sub>x</sub> S <sub>y</sub> @MnO <sub>x</sub> H <sub>y</sub>	1.53	1 M KOH	68
<sup>nb</sup> CuNC <sub>3</sub> <sup>OER</sup> //CoN <sub>0.73</sub> Co <sub>3</sub> <sup>HER</sup>	1.53	1 M KOH	107
CoN@NC	1.53	1 M KOH	106
Co <sub>0.21</sub> Fe <sub>0.28</sub> (OH)F	1.53	1 M KOH	130
P-CoMoO <sub>4</sub>	1.54	1 M KOH	40
NiCoFe-P/C	1.55	1 M KOH	93
Co <sub>2</sub> P/Mo <sub>2</sub> C@NC	1.55	1 M KOH	121
Ni <sub>3</sub> S <sub>2</sub> /FeNi <sub>2</sub> S <sub>4</sub>	1.55	1 M KOH	66

<sup>a</sup> nb: non-bifunctional electrocatalyst; c-NiFe/a-NiFeOOH@NiMo: crystalline-NiFe/amorphous-NiFeOOH@NiMo; CNTs: carbon nanotubes; LDH: layered double hydroxide; c-CoMnP/a-CoMn LDH: crystalline CoMnP decorated amorphous CoMn LDH; c-CoFeP/a-CoFe LDH: crystalline CoFeP decorated amorphous CoFe LDH; VSB/NiPO: nickel phosphate micropism, where the micropism is mainly composed of Versailles-Santa Barbara-5, which is a kind of nickel phosphate molecular sieve having the chemical formula of Ni<sub>20</sub>[(OH)<sub>12</sub>(H<sub>2</sub>O)<sub>6</sub>][(HPO<sub>4</sub>)<sub>8</sub>(PO<sub>4</sub>)<sub>4</sub>]·12H<sub>2</sub>O; MH-TMO: mesoporous and heterostructured transition metal oxides; M-Co-CN: it was synthesized by the heat treatment of modified-ZIF-67 followed by acid treatment, where ZIF-67 represents the Co-based zeolitic imidazolate framework; act-modified-ZIF-67: activated modified Co-based zeolitic imidazolate framework; hnsa: hybrid nanosheet array; Gr: graphene. <sup>b</sup> ~1.45 V at 50 mA cm<sup>-2</sup>.



**Table 12** Potential (Part 2: potential from 1.56 to 1.87 V) to achieve 10 mA cm<sup>-2</sup> for overall water splitting of different kinds of reported non-noble metal bifunctional electrocatalysts in an alkaline electrolyte<sup>a</sup>

Bifunctional electrocatalysts for the HER and OER	Overall water splitting (V at 10 mA cm <sup>-2</sup> )	Electrolyte	Ref.
Ni/CeO <sub>2</sub> @N-CNFs	1.56	1 M KOH	42
Fe,Ce-Ni <sub>x</sub> S <sub>y</sub>	1.56	1 M KOH	61
Mo <sub>2</sub> C-CoO@NC	1.56	1 M KOH	120
Ni <sub>2</sub> P-Fe <sub>2</sub> P	1.561	1 M KOH	19
LSC-N-GQDs-MoSe <sub>2</sub>	~1.57	1 M KOH	80
W-NiS <sub>2</sub> /MoO <sub>2</sub>	1.57	1 M KOH	63
CoP-NC@NiFeP	1.57	1 M KOH	98
Cu <sub>3</sub> P-Cu <sub>2</sub> O/NPC	1.57	1 M KOH	100
Co-Ni <sub>3</sub> S <sub>2</sub>	1.58	1 M KOH	59
Fe-NiS-NiS <sub>2</sub>	1.59	1 M KOH	62
<sup>nb</sup> act-Ni-CoP/Co <sub>2</sub> P@NC <sup>OER</sup> //Ni-CoP/Co <sub>2</sub> P@NC <sup>HER</sup>	1.59	1 M KOH	97
Co/Mo <sub>2</sub> C@C	1.59	1 M KOH	118
Hea-d48h	1.615	1 M KOH	125
<sup>nb</sup> SAE <sub>OER</sub> -ECT-NiSi <sup>OER</sup> //SAE <sub>HER</sub> -ECT-NiSi <sup>HER</sup>	1.63 <sup>b</sup>	1 M KOH	132
<sup>nb</sup> Fe/Mo <sub>2</sub> C-NC <sup>OER</sup> //Ni/Mo <sub>2</sub> C-NC <sup>HER</sup>	1.66 <sup>c</sup>	1 M KOH	117
Ni <sub>3</sub> Fe <sub>0.75</sub> V <sub>0.25</sub> /Ni <sub>3</sub> Fe <sub>0.75</sub> V <sub>0.25</sub> N	1.66	1 M KOH	129
Ni <sub>3</sub> S <sub>2</sub> -MoS <sub>2</sub>	1.67	1 M KOH	65
Ce@NiCo LDH	1.68	1 M KOH	55
Co-Mn-CO <sub>3</sub> -OH	1.68	1 M KOH	48
MoO <sub>2</sub> /Co	1.683	1 M KOH	30
Ni-FePS <sub>3</sub>	1.71	1 M KOH	71
Co <sub>2</sub> N <sub>0.67</sub> /CoMoO <sub>4</sub>	1.71 <sup>d</sup>	1 M KOH	20
Fe <sub>2</sub> P/Co@NPC	1.73	1 M KOH	6e
e-FeCoNiCu-P	1.738 <sup>e</sup>	1 M KOH	89
CoNiP	~1.76 <sup>f</sup>	1 M KOH	84
Zn-Fe/Mn@Mn-FeP	1.79 <sup>g</sup>	1 M KOH	28
<sup>nb</sup> NiFe LDH <sup>OER</sup> //Ni <sub>2</sub> P <sup>HER</sup>	~1.8 <sup>h</sup>	1 M KOH	82
Ni/MoO <sub>2</sub> @CN	1.83 <sup>i</sup>	1 M KOH	15
Co-Ni <sub>3</sub> S <sub>2</sub>	1.87 <sup>j</sup>	1 M NaOH	58

<sup>a</sup> nb: non-bifunctional electrocatalyst; N-CNFs: N-doped carbon nanofibers; LDH: layered double hydroxide; e-FeCoNiCu-P: electrochemically etched FeCoNiCu-P; LSC/LSCO: La<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3-δ</sub>; N-GQDs: N-doped graphene quantum dots; hea-d48h: it is a high-entropy alloy (hea), which is de-alloyed for 48 h, where the Ni<sub>30</sub>Co<sub>30</sub>Cr<sub>10</sub>Fe<sub>10</sub>Al<sub>18</sub>W<sub>2</sub> high-entropy alloy comprises FCC and ordered aluminum-enriched BCC phases, while three dimensional porous architecture is constructed by de-alloying (selective etching of the BCC phase) the high-entropy alloy for 48 h; SAE<sub>HER</sub>-ECT-NiSi: NiSi is subjected to ECT followed by SAE<sub>HER</sub>, where ECT is an electrochemical tuning process comprising lithiation and rapid delithiation of NiSi, while SAE<sub>HER</sub> is a self-adaptive evolution that involves conducting multiple linear sweep voltammetry on ECT-NiSi under HER conditions; SAE<sub>OER</sub>-ECT-NiSi: NiSi is subjected to ECT followed by SAE<sub>OER</sub>, where ECT is an electrochemical tuning process comprising lithiation and rapid delithiation of NiSi, while SAE<sub>OER</sub> is a self-adaptive evolution that involves conducting multiple linear sweep voltammetry on ECT-NiSi under OER conditions; act-Ni-CoP/Co<sub>2</sub>P@NC: activated Ni-CoP/Co<sub>2</sub>P@NC. <sup>b</sup> 1.63 V at 100 mA cm<sup>-2</sup>. <sup>c</sup> 1.66 V at 100 mA cm<sup>-2</sup>. <sup>d</sup> 1.71 V at 100 mA cm<sup>-2</sup>. <sup>e</sup> 1.738 V at 100 mA cm<sup>-2</sup>. <sup>f</sup> ~1.76 V at 20 mA cm<sup>-2</sup>. <sup>g</sup> 1.79 V at 50 mA cm<sup>-2</sup>. <sup>h</sup> ~1.8 V at 250 mA cm<sup>-2</sup>. <sup>i</sup> 1.83 V at 200 mA cm<sup>-2</sup>. <sup>j</sup> 1.87 V at 20 mA cm<sup>-2</sup>.

reported noble-metal-free electrocatalysts for the OER in alkaline electrolytes. Tables 11 and 12 provide the potential to achieve 10 mA cm<sup>-2</sup> for overall water splitting of different kinds of reported noble-metal-free bifunctional electrocatalysts in alkaline electrolytes. Tables 13 and 14 provide the long-term stability of various reported noble-metal-free electrocatalysts for overall water splitting in alkaline electrolytes. Table 15 provides the overpotential to achieve -1000 mA cm<sup>-2</sup> for the HER of various reported noble-metal-free electrocatalysts in alkaline electrolytes. Table 16 provides the overpotential to achieve 1000 mA cm<sup>-2</sup> for the OER of various reported noble-metal-free electrocatalysts in alkaline

electrolytes. Table 17 provides the potential to achieve 1000 mA cm<sup>-2</sup> for overall water splitting of different kinds of reported noble-metal-free bifunctional electrocatalysts in alkaline electrolytes.

### 3 Summary and outlook

One of the promising approaches for generating hydrogen is electrochemical water splitting. At the same time, efficient water-splitting can be achieved by developing noble metal-free electrocatalysts for the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER). The activity, stability, and durability of several kinds of recently reported noble



**Table 13** Long-term stability (Part 1: 50 h to 500 h of duration) of various reported noble metal-free electrocatalysts for overall water splitting in 1 M KOH alkaline electrolyte<sup>a</sup>

Bifunctional electrocatalysts for the HER and OER	Chr amp	Chr pot	Dur (h)	Remark after the stability test	Ref.
<sup>nb</sup> OR-NiOOH <sup>OER</sup> //HR-NiMoO@Ni <sup>HER</sup>	NA	Yes	500	Reasonable stability at a CD of 1000 A m <sup>-2</sup>	38
NiFeLa LDH/v-MXene	NA	Yes	400	Negligible decay at a CD of 100 mA cm <sup>-2</sup>	57
<sup>nb</sup> act-Ni-CoP/Co <sub>2</sub> P@NC <sup>OER</sup> //Ni-CoP/Co <sub>2</sub> P@NC <sup>HER</sup>	Yes	NA	400	Negligible decay at a potential of 1.6 V	97
Ni/MoO <sub>2</sub> @CN	NA	Yes	300	Negligible decay at a CD of 1000 mA cm <sup>-2</sup>	15
Cu <sub>3</sub> P-Cu <sub>2</sub> O/NPC	Yes	NA	168	98.19% retention at a potential of 1.7 V	100
Ni <sub>x</sub> S <sub>y</sub> @MnO <sub>x</sub> H <sub>y</sub>	NA	Yes	100	Negligible decay at a CD of 100 mA cm <sup>-2</sup>	68
c-NiFe/a-NiFeOOH@NiMo	NA	Yes	100	95.86% retention at a CD of 100 mA cm <sup>-2</sup>	11
<sup>nb</sup> Fe-VSB/NiPO-500 <sup>OER</sup> //VSB/NiPO <sup>HER</sup>	NA	Yes	100	96.44% retention at a CD of 100 mA cm <sup>-2</sup>	105
MH-TMO	NA	Yes	100	Negligible decay at a CD of 10 mA cm <sup>-2</sup>	1g
Hea-d48h	Yes	NA	100	99.13% retention	125
Ni/CeO <sub>2</sub> @N-CNFs	Yes	NA	100	Negligible decay	42
WCoSe/WCo <sub>3</sub> O <sub>4</sub>	NA	Yes	100	Reasonable stability at a CD of 100 mA cm <sup>-2</sup>	78
<sup>nb</sup> act-modified-ZIF-67 <sup>OER</sup> //M-Co-CN <sup>HER</sup>	NA	Yes	100	93.7% retention at a CD of 20 mA cm <sup>-2</sup>	114
Fe,Ce-Ni <sub>x</sub> S <sub>y</sub>	NA	Yes	90	Reasonable stability at a CD of 20 mA cm <sup>-2</sup>	61
<sup>nb</sup> c-CoFeP/a-CoFe LDH <sup>OER</sup> //c-CoMnP/a-CoMn LDH <sup>HER</sup>	NA	Yes	85	29.1 mV decay at a CD of 100 mA cm <sup>-2</sup>	56
Zn-Fe/Mn@Mn-FeP	NA	Yes	80	Reasonable stability at a CD of 50 mA cm <sup>-2</sup>	28
P-CoMoO <sub>4</sub>	NA	Yes	72	Negligible decay at a CD of 50 mA cm <sup>-2</sup>	40
Sn-Ni <sub>3</sub> S <sub>2</sub>	Yes	NA	~70	Negligible decay at a potential of 2.26 V	14
Gr-CNTs-Sn <sub>4</sub> P <sub>3</sub>	Yes	NA	65	96% retention at a potential of 1.482 V	12
Fe <sub>2</sub> P/Co@NPC	NA	Yes	60	Reasonable stability at a CD of 10 mA cm <sup>-2</sup>	6e
<sup>nb</sup> SAE <sup>OER</sup> -ECT-NiSi <sup>OER</sup> //SAE <sup>HER</sup> -ECT-NiSi <sup>HER</sup>	Yes	NA	55	Negligible decay at a potential of 1.75 V	132
NiS/MoS <sub>2</sub>	Yes	NA	50	99.2% retention	64
NiP <sub>2</sub> /NbP@CNTs	Yes	NA	50	Negligible decay	96
Co <sub>2</sub> N <sub>0.67</sub> /CoMoO <sub>4</sub>	NA	Yes	50	Reasonable stability at a CD of 500 mA cm <sup>-2</sup>	20
Mn <sub>1</sub> Ni <sub>1</sub> Co <sub>1</sub> -P	Yes	NA	50	96% retention at a potential of 1.48 V	10
Ni <sub>3</sub> S <sub>2</sub> /FeNi <sub>2</sub> S <sub>4</sub>	Yes	NA	50	Negligible decay at a potential of 2 V	66
Fe-CoP	NA	Yes	50	Negligible decay at a CD of 10 mA cm <sup>-2</sup>	85

<sup>a</sup> Ref.: references; Dur: duration of the stability test; Chr pot: chronopotentiometry; Chr amp: chronoamperometry; NA: not applicable; CD: current density; c-NiFe/a-NiFeOOH@NiMo: crystalline-NiFe/amorphous-NiFeOOH@NiMo; CNTs: carbon nanotubes; LDH: layered double hydroxide; c-CoMnP/a-CoMn LDH: crystalline CoMnP decorated amorphous CoMn LDH; c-CoFeP/a-CoFe LDH: crystalline CoFeP decorated amorphous CoFe LDH; VSB/NiPO: nickel phosphate microprism, where the microprism is mainly composed of Versailles-Santa Barbara-5, which is a kind of nickel phosphate molecular sieve having the chemical formula of Ni<sub>20</sub>[(OH)<sub>12</sub>(H<sub>2</sub>O)<sub>6</sub>][(HPO<sub>4</sub>)<sub>8</sub>(PO<sub>4</sub>)<sub>4</sub>·12H<sub>2</sub>O]; MH-TMO: mesoporous and heterostructured transition metal oxides; hea-d48h: it is a high-entropy alloy (hea), which is de-alloyed for 48 h, where the Ni<sub>30</sub>Co<sub>30</sub>Cr<sub>10</sub>Fe<sub>10</sub>Al<sub>18</sub>W<sub>2</sub> high-entropy alloy comprises FCC and ordered aluminum-enriched BCC phases, while three dimensional porous architecture is constructed by de-alloying (selective etching of the BCC phase) the high-entropy alloy for 48 h; SAE<sup>HER</sup>-ECT-NiSi: NiSi is subjected to ECT followed by SAE<sup>HER</sup>, where ECT is an electrochemical tuning process comprising lithiation and rapid delithiation of NiSi, while SAE<sup>HER</sup> is a self-adaptive evolution that involves conducting multiple linear sweep voltammetry on ECT-NiSi under HER conditions; SAE<sup>OER</sup>-ECT-NiSi: NiSi is subjected to ECT followed by SAE<sup>OER</sup>, where ECT is an electrochemical tuning process comprising lithiation and rapid delithiation of NiSi, while SAE<sup>OER</sup> is a self-adaptive evolution that involves conducting multiple linear sweep voltammetry on ECT-NiSi under OER conditions; N-CNFs: N-doped carbon nanofibers; act-Ni-CoP/Co<sub>2</sub>P@NC: activated Ni-CoP/Co<sub>2</sub>P@NC; M-Co-CN: it was synthesized by the heat treatment of modified-ZIF-67 followed by acid treatment, where ZIF-67 represents the Co-based zeolitic imidazolate framework; act-modified-ZIF-67: activated modified Co-based zeolitic imidazolate framework; Gr: graphene; nb: non-bifunctional electrocatalyst.

metal-free electrocatalysts such as oxides/hydroxides/(oxy) hydroxides/layered double hydroxides, sulfides, selenides, phosphides/phosphates, nitrides, carbon-based electrocatalysts, and alloy/B/V/F/Si based electrocatalysts for the HER and OER in an alkaline environment have been reviewed in this paper. In addition, this paper reviews the strategies used to achieve high activity and stability/durability, including at a high current density of  $\geq 1000$  mA cm<sup>-2</sup> of noble metal-free electrocatalysts for the HER and OER in an alkaline environment.

The following several promising strategies have been used for the noble metal-free electrocatalysts to attain enhanced performance for the HER and/or OER in alkaline environments (Fig. 9):

(a) Fabricating oxide based noble metal-free electrocatalysts enhanced the performance for the HER and OER, while various strategies including preparing ultrathin/nanostructures, creating oxygen vacancies, creating heterojunctions, doping of metals/non-metals, preparing transition bimetallic oxide based catalysts, facet engineering, creating high valence ions,



**Table 14** Long-term stability (Part 1: 12 h to 48 h of duration) of various reported noble metal-free electrocatalysts for overall water splitting in 1 M KOH alkaline electrolyte, where the electrolyte other than 1 M KOH is indicated on the electrocatalyst<sup>a</sup>

Bifunctional electrocatalysts for the HER and OER	Chr amp	Chr pot	Dur (h)	Remark after the stability test	Ref.
1T Co-WS <sub>2</sub> /NiTe <sub>2</sub> /Ni	Yes	NA	48	94% retention	73
<sup>nb</sup> CuNC <sub>3</sub> <sup>OER</sup> //CoN <sub>0.73</sub> Co <sub>3</sub> <sup>HER</sup>	Yes	NA	48	90% retention	107
Co/Mo <sub>2</sub> C@C	Yes	NA	48	90.2% retention at a potential of 1.59 V	118
Ni <sub>3</sub> Fe <sub>0.75</sub> V <sub>0.25</sub> /Ni <sub>3</sub> Fe <sub>0.75</sub> V <sub>0.25</sub> N	Yes	NA	40	Reasonable stability at a potential of 2 V	129
CoP-NC@NiFeP	NA	Yes	40	Reasonable stability at a CD of 50 mA cm <sup>-2</sup>	98
Fe <sub>2</sub> P-CoP/CeO <sub>2</sub>	NA	Yes	40	Reasonable stability at a CD of 500 mA cm <sup>-2</sup>	101
Ni <sub>2</sub> P-Fe <sub>2</sub> P	NA	Yes	>40	Reasonable stability at a CD of 500 mA cm <sup>-2</sup>	19
FeP/Ni <sub>2</sub> P	NA	Yes	>40	Negligible decay at a CD of 500 mA cm <sup>-2</sup>	18
Ce@NiCo LDH	Yes	NA	36	Reasonable stability at a potential of 1.68 V	55
Co <sub>2</sub> P/Mo <sub>2</sub> C@NC	Yes	NA	30	Negligible decay	121
Fe@Co/Se <sub>2</sub>	NA	Yes	30	Negligible decay at a CD of 10 mA cm <sup>-2</sup>	77
Co-Ni <sub>3</sub> S <sub>2</sub>	Yes	NA	30	Negligible decay at a potential of 1.58 V	59
Mn <sub>6</sub> -CoO	NA	Yes	28	Reasonable stability at a CD of 10 mA cm <sup>-2</sup>	31
CoN@NC	NA	Yes	25	Reasonable stability at a CD of 10 mA cm <sup>-2</sup>	106
Mo <sub>2</sub> C-CoO@NC	Yes	NA	>25	Reasonable stability at a potential of 1.9 V	120
NiCoFe-P/C	Yes	NA	24	Reasonable stability	93
e-FeCoNiCu-P	NA	Yes	24	Negligible decay at a CD of 100 mA cm <sup>-2</sup>	89
LSC-N-GQDs-MoSe <sub>2</sub>	NA	Yes	24	Negligible decay at a CD of 500 mA cm <sup>-2</sup>	80
<sup>nb</sup> S-NiFeP-10 <sup>OER</sup> //S-NiFeP-20 <sup>HER</sup>	Yes	NA	24	Reasonable stability at a potential of 1.5 V	91
Co-Ni <sub>3</sub> S <sub>2</sub> <sup>1 M NaOH</sup>	NA	Yes	24	Negligible decay	58
<sup>nb</sup> Fe/Mo <sub>2</sub> C-NC <sup>OER</sup> //Ni/Mo <sub>2</sub> C-NC <sup>HER</sup>	Yes	NA	24	Reasonable stability at a potential of 1.66 V	117
Co <sub>0.21</sub> Fe <sub>0.28</sub> (OH)F	NA	Yes	20	Negligible decay at a CD of 20 mA cm <sup>-2</sup>	130
NiMoB hollow foam	NA	Yes	20	Reasonable stability at a CD of 5000 mA cm <sup>-2</sup>	8
<sup>nb</sup> NiFe LDH <sup>OER</sup> //Ni <sub>2</sub> P <sup>HER</sup>	Yes	NA	>15	Reasonable stability at a potential of 2.1 V	82
NiCoP	Yes	NA	12	98% retention	83
Fe-NiS-NiS <sub>2</sub>	Yes	NA	12	Reasonable stability at a potential of 1.59 V	62
Co-Mn-CO <sub>3</sub> -OH	NA	Yes	>12	Negligible decay at a CD of 10 mA cm <sup>-2</sup>	48

<sup>a</sup> nb: non-bifunctional electrocatalyst; Ref.: references; Dur: duration of the stability test; Chr pot: chronopotentiometry; Chr amp: chronoamperometry; NA: not applicable; CD: current density; LDH: layered double hydroxide; e-FeCoNiCu-P: electrochemically etched FeCoNiCu-P; LSC/LSCO: La<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3-δ</sub>; N-GQDs: N-doped graphene quantum dots.

**Table 15** Overpotential ( $\eta$ ) to achieve  $-1000 \text{ mA cm}^{-2}$  for the hydrogen evolution reaction (HER) of various reported noble metal-free electrocatalysts in an alkaline electrolyte<sup>a</sup>

HER electrocatalysts	$\eta$ at $-1000 \text{ mA cm}^{-2}$ (mV)	Electrolyte	Ref.
MoS <sub>2</sub> /Mo <sub>2</sub> C	-220	1 M KOH	21
C-Ni <sub>1-x</sub> O/3D printed Ni	-245	1 M KOH	16
Fe-Co-CO <sub>3</sub> -OH	-256	1 M KOH	17
Ni/MoO <sub>2</sub> @CN	-267	1 M KOH	15
FeP/Ni <sub>2</sub> P	~-270	1 M KOH	18
Ni <sub>2</sub> (1-x)Mo <sub>2x</sub> P	-294	1 M KOH	86
Ni <sub>2</sub> P	-306	1 M KOH	82
HR-NiMoO@Ni	-308	1 M KOH	38
Mo <sub>5</sub> N <sub>6</sub> -MoS <sub>2</sub> -HCNRs	-315	1 M KOH	108
Co <sub>2</sub> N <sub>0.67</sub> /CoMoO <sub>4</sub>	-315	1 M KOH	20
Ni <sub>2</sub> P-Fe <sub>2</sub> P	-333	1 M KOH	19
NiP <sub>2</sub> -FeP <sub>2</sub> @Cu nanoarray	-357	1 M KOH	13
NiMoB hollow foam	~-420	1 M KOH	8
Sn-Ni <sub>3</sub> S <sub>2</sub>	-570	1 M KOH	14
Co-Ni <sub>3</sub> S <sub>2</sub>	-850	1 M KOH	59

<sup>a</sup> HCNRs: hollow carbon nanoribbons.

integrating with carbon, designing the facile synthesis route, and utilization of waste enhanced the performance.<sup>1g,15-16,27,29-42</sup>

(b) Fabricating hydroxide based noble metal-free electrocatalysts enhanced the performance for the HER and OER, while various strategies including preparing nanostructures, preparing transition bimetallic carbonate hydroxides, increasing the conductivity and electrochemical surface area, creating abundant oxygen vacancies, doping of metals, and developing facile synthesis routes at ambient temperature enhanced the performance.<sup>17,26,43-48</sup>

(c) Fabricating (oxy)hydroxide based noble metal-free electrocatalysts enhanced the performance for the HER and OER, while various strategies including creating abundant defects, generating multiple vacancies, doping of elements, developing NiFe based catalysts, and developing facile synthesis routes enhanced the performance.<sup>6a,11,24,49-50</sup>

(d) Fabricating layered double hydroxide based noble metal-free electrocatalysts enhanced the performance for the HER and OER, while various strategies including electrochemical activation, doping of metals, preparing heterostructures, integrating with MXene/metal nanoparticles and developing facile synthesis routes enhanced the performance.<sup>25,51-57</sup>



**Table 16** Overpotential ( $\eta$ ) to achieve 1000 mA cm<sup>-2</sup> for the oxygen evolution reaction (OER) of various reported noble metal-free electrocatalysts in an alkaline electrolyte ( $\eta$  to achieve greater than 1000 mA cm<sup>-2</sup> is mentioned on the  $\eta$ , which is described in the footnote of this table)<sup>a</sup>

OER electrocatalysts	$\eta$ at 1000 mA cm <sup>-2</sup> (mV)	Electrolyte	Ref.
FeP/Ni <sub>2</sub> P	293	1 M KOH	18
Fe-Co-CO <sub>3</sub> -OH	308	1 M KOH	17
Ni <sub>2</sub> P-Fe <sub>2</sub> P	337	1 M KOH	19
OR-NiOOH	358	1 M KOH	38
KT-Ni(0)@Ni(II)-TPA	380 <sup>b</sup>	1 M KOH	112
Ni/MoO <sub>2</sub> @CN	420	1 M KOH	15
C-Ni <sub>1-x</sub> O/3D printed Ni	425	1 M KOH	16
Fe-CoP	428	1 M KOH	85
NiMoB hollow foam	~460	1 M KOH	8
Co-Mn-CO <sub>3</sub> -OH	462	1 M KOH	48
(Ni-Fe) <sub>2</sub> S <sub>4</sub> /NiFe(OH) <sub>y</sub>	~510	1 M KOH	69
CuS-Ni <sub>3</sub> S <sub>2</sub> /CuNi	510	1 M KOH	22
Sn-Ni <sub>3</sub> S <sub>2</sub>	580	1 M KOH	14
Co-Ni <sub>3</sub> S <sub>2</sub>	750	1 M KOH	59
Ce-NiFe	~770	1 M KOH	47

<sup>a</sup>  $\eta$ : overpotential; KT-Ni(0)@Ni(II)-TPA: a terephthalic acid (TPA)-regulated etching strategy is used for the preparation of a karst topography (KT) featured electrode containing core-shell structured Ni(0)@Ni(II)-TPA. <sup>b</sup> 380 mV at 1500 mA cm<sup>-2</sup>.

**Table 17** Potential to achieve 1000 mA cm<sup>-2</sup> for overall water splitting of different kinds of reported non-noble metal bifunctional electrocatalysts in alkaline electrolyte<sup>a</sup>

Bifunctional electrocatalysts for the HER and OER	Overall water splitting (V at 1000 mA cm <sup>-2</sup> )	Electrolyte	Ref.
FeP/Ni <sub>2</sub> P	~1.78	1 M KOH	18
Ni <sub>2</sub> P-Fe <sub>2</sub> P	~1.98	1 M KOH	19
Co <sub>2</sub> N <sub>0.67</sub> /CoMoO <sub>4</sub>	1.98	1 M KOH	20
Ni/MoO <sub>2</sub> @CN	2.02	1 M KOH	15
<sup>nb</sup> NiFe LDH <sup>OER</sup> //Ni <sub>2</sub> P <sup>HER</sup>	~2.05	1 M KOH	82
Sn-Ni <sub>3</sub> S <sub>2</sub>	~2.65	1 M KOH	14
NiMoB hollow foam	~3.8	1 M KOH	8

<sup>a</sup> nb: non-bifunctional electrocatalyst.

(e) Fabricating sulfide based noble metal-free electrocatalysts enhanced the performance for the HER and OER, while various strategies including preparing ultrathin/nanostructures, preparing amorphous sulfide based catalysts, doping of metals, preparing heterojunctions/heterostructures, creating super-aerophobic surfaces, creating high valence state sites, creating abundant bridging S<sub>2</sub><sup>2-</sup> sites, and developing facile synthesis routes enhanced the performance.<sup>14,22,58-75</sup>

(f) Fabricating selenide based noble metal-free electrocatalysts enhanced the performance for the HER and OER, while various strategies including preparing nanostructures, creating heterostructures, doping of metals, and activation of the inert basal plane enhanced the performance.<sup>9,76-81</sup>

(g) Fabricating phosphide/phosphate based noble metal-free electrocatalysts enhanced the performance for the HER and OER, while various strategies including preparing nanostructures/nanoporous, creating heterostructures/core-shell structures, integrating with carbon, preparing bimetallic/tri-metallic, increasing the conductivity and electrochemical surface area, creating superaerophobic surfaces, and developing facile and scalable synthesis routes enhanced the performance.<sup>6e,10,13,18-19,28,82-93,95-105</sup>

(h) Fabricating nitride based noble metal-free electrocatalysts enhanced the performance for the HER and OER, while various strategies including preparing nanostructures/porous structures, doping of elements, and preparing heterojunctions/heterostructures enhanced the performance.<sup>20,106-110</sup>

(i) Fabricating carbon based noble metal-free electrocatalysts enhanced the performance for the HER and OER, while various strategies including creating nanostructures/porous structures/heterostructures/core-shell structures, creating super-aerophobic surfaces, doping of elements, and creating abundant low-coordinate Co-N sites enhanced the performance.<sup>21,111-121</sup>

(j) Fabricating alloy/B/V/F/Si based noble metal-free electrocatalysts enhanced the performance for the HER and OER, while various strategies including preparing nanostructures/heterostructures/heterojunctions/hollow structures/ultrathin structures/porous structures/creating high valence sites, electrochemical activation, and designing facile synthesis routes enhanced the performance.<sup>8,122-132</sup>

The stage has been developed for the noble metal-free electrocatalysts for the HER and OER to afford superior performance in practical applications. Hence, the vital factors governing the performance of noble metal-free electrocatalysts should be considered in future research: (1) recently, some green chemistry approaches, including ambient temperature synthesis,<sup>24-26</sup> utilization of waste as a source,<sup>27</sup> and using relatively low-cost metals,<sup>28</sup> have been used for the fabrication of noble metal-free electrocatalysts for electrochemical water splitting. However, efficient green chemistry approaches for fabricating efficient noble metal-free electrocatalysts for the HER and OER are considerably limited. Hence, more progress is needed to construct efficient noble metal-free electrocatalysts for the HER and OER using various green chemistry approaches.

(2) Noble metal-free bifunctional electrocatalysts for overall water splitting exhibit low cell voltage at much higher current densities with high stability, which are substantially minimal. Therefore, additional progress is obviously needed to fulfill the requirement of industrial water electrolysis.



## Strategies used to enhance the performance for HER and/or OER of noble-metal-free electrocatalysts

### 1. Oxide based electrocatalysts:

Preparing ultrathin/nanostructure, creating oxygen vacancies, creating heterojunction, doping of metal/non-metal, preparing transition bimetal based, facet engineering, creating high valence ions, integrating with carbon, designing the facile synthesis route, and utilization of waste.

### 2. Hydroxide based electrocatalysts:

Preparing nanostructure, preparing transition bimetallic carbonate hydroxides, increasing conductivity and electrochemical surface area, creating abundant oxygen vacancies, doping of metal, and developing facile synthesis route at ambient temperature.

### 3. (Oxy)hydroxide based electrocatalysts:

Creating abundant defects, generating multiple vacancies, doping of elements, developing NiFe based catalysts, and developing facile synthesis route.

### 4. Layered double hydroxide based electrocatalysts:

Electrochemical activation, doping of metal, preparing heterostructure, integrating with MXene/metal nanoparticles and developing facile synthesis route.

### 5. Sulfide based electrocatalysts:

Preparing ultrathin/nanostructure, preparing amorphous, doping of metal, preparing heterojunctions/heterostructure, creating super-aerophobic surface, creating high valence state sites, creating abundant bridging  $S_2^{2-}$  sites, and developing facile synthesis route.

### 6. Selenide based electrocatalysts:

Preparing nanostructure, creating heterostructure, doping of metals, and activation of the inert basal plane.

### 7. Phosphide/phosphate based electrocatalysts:

Preparing nanostructure/nanoporous, creating heterostructure/core-shell structure, integrating with carbon, preparing bimetallic/trimetallic, increasing conductivity and electrochemical surface area, creating superaerophobic surface, and developing facile and scalable synthesis route.

### 8. Nitride based electrocatalysts:

Preparing nanostructure/porous structure, doping of elements, and preparing heterojunction/heterostructure.

### 9. Carbon based electrocatalysts:

Creating nanostructure/porous structure/heterostructure/core-shell structure, creating superaerophobic surface, doping of elements, and creating abundant low-coordinate Co–N sites.

### 10. Alloy/B/V/F/Si based electrocatalysts:

Preparing nanostructure/heterostructure/heterojunction/hollow structure/ultrathin structure/porous structure/ creating high valence sites, electrochemical activation, and designing facile synthesis route.

Fig. 9 Strategies used to enhance the performance for the HER and/or OER of noble metal-free electrocatalysts.

## Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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